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DTM-Decom III - Intercomparison exercise in analysis of DTM beta and gamma emitters in spent ion exchange resin

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Abstract

An intercomparison exercise was carried out for difficult to measure beta radionuclides in spent ion exchange resin samples. The results were analysed according to the ISO 13528 standard. The performance assessment was carried out using z score. The report includes an overview of the radioanalytical procedures, preliminary and final results, and performance assessments.

Key words

Decommissioning, Difficult-to-measure radionuclides, intercomparison exercise, spent ion exchange resin

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Final Report from the NKS-B DTM-Decom III activity

(Contract: AFT/B(21)2)

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1. Introduction to DTM Decom III

The first two years of three year DTM Decom project have shown that validation of radiochemical analysis of difficult-to-measure (DTM) radionuclides in decommissioning waste is important. The DTM Decom I project (2019) was an intercomparison exercise on DTMs in activated steel. The results were published as an NKS report [Leskinen et al. 2020b] and in the Journal of Radioanalytical and Nuclear Chemistry (JRNC) together with activation calculation results [Leskinen et al. 2020c]. DTM Decom II project (2020) concentrated on DTM analysis in activated concrete. The results were published as an NKS report [Leskinen et al. 2021a] and in the JRNC together with modelling results [Leskinen et al. 2021b].

In 2021, the DTM Decom III project studied DTMs in a spent ion exchange resin sample. In primary circuit, radionuclides originate from corrosion and leaked fuel causing a wide mixture of radionuclides in the spent ion exchange resin. The project consortium decided in the kick-off meeting that the main DTMs were Fe-55 and Ni-63 (corrosion products) and Sr-90 (fuel originated radionuclide). Optional DTMs were H-3, C-14, Cl-36 and Ni-59 whereas capabilities for Tc-99, I-129 and Cs-135 analysis were also indicated. Even though the previously studied materials, namely steel and concrete, contained some gamma emitters, the spectrum of gamma emitters in the spent ion exchange resin was expected to be wide as the resin sample was quite fresh containing short living radionuclides such as Mn-54 and both corrosion products such as Co-60 and fission products such as Cs-137. Similarly to the first two years, the DTM Decom III intercomparison exercise was carried out according to ISO 13528 standard [International Standard 2015]. The homogeneities of the studied ion exchange resin samples were determined using gamma spectrometry and Cs-137 as a reference radionuclide. The analysis time schedule was from May/June until October when a preliminary meeting was held in order to discuss the analysis results and difficulties in the DTM analyses. After the preliminary meeting, partners had the possibility to re-evaluate their results and carry out further experiments until November when the final meeting was held. Both the preliminary and final results are presented in this report.

This report presents the references used in the DTM analysis of spent ion exchange resin, overview of the radiochemical methods, measurement results and statistical analysis of the results.

2. Survey of capabilities in the beginning of the project

A survey of the DTM analysis capabilities of the participating laboratories in the beginning of the project are shown in Table 1. The results show that some laboratories were well advanced with several methods ready for DTM analyses whereas some laboratories were in the method development phase. The sample numbers in following sections do not correspond to the affiliation order in Table 1 (i.e., anonymous reporting).

Table 1. Capabilities of the participating laboratories on analysis of DTMs in spent ion exchange resin in the beginning of the project

Affiliation code	Capabilities in DTM analyses
A	Method under development. National project on going for analysis H-3, C-14, Fe-55, Ni-63, Sr-90 in spent resin. Method development for Cl-36 and Ni-59 ongoing, perhaps will be utilised in this project.
B	Method under development for analysis of Fe-55 and Ni-63 in an ion exchange resin. Methods for determination of Sr-90, U- and Pu-isotopes are ready to be used.
C	Methods for determination of H-3, C-14, Cl-36, Fe-55, Ni-63, Sr-90, Tc-99, I-129, Cs-135 and actinides (U, Pu, Np, Am, Cm) in resin are ready to be used, The speciation analysis methods for H-3, C-14 in resin are also ready to be used.
D	Routine analysis for H-3, C-14, Fe-55, Ni-63, Cl-36 and Ca-41 in radioactive samples at low and intermediate level activity (liquids, effluents, concretes and resins).
E	Participant in an on-going national project for analysis of Fe-55,Ni-63 Sr-90 in spent resin.
F	Currently building capacity for nuclides of significance for national nuclear decommissioning challenges, specifically Ca-41, Ni-59, Ni-59, Se-79, Zr-93, Tc-99, Pd-107, Sn-126, Cs-135, uranium, neptunium, plutonium & co.
G	Routine capabilities include Ni-63 and Fe-55 measurements from spent resin, evaporator waste and swipe samples. Method is also found to be suitable for analysis in stainless steel from NPPs with sample pretreatment different than for the routine analysis.
H	Method under development for analysis of Fe-55 and Ni-63 in an ion exchange resin. Methods for analysis of Sr-90 already in place. Methods for analysis of Pu and other alpha-emitters under development.
J	Routine capabilities include H-3, C-14, Fe-55, Ni-63, Sr-90, Am-241, I-129, Tc-99, Pu-238, Pu239/240, Pu241, Cm-242, Cm-244 in spent resin sample.

3. Preparation, homogeneity and sending of the samples

Approximately 0.8 g of spent ion exchange resin (FINEX C/A 850 H mixed exchanger in powder form, nuclear grade) were weight in nine glass liquid scintillation vials (Figure 1). The surface dose rate was approximately 30 μSv/h. Each sample was measured twice by placing them 20 cm distance from top of an HPGe detector of an ISOCS counting system for 15 minutes. Constant measurement geometry was ensured by placing the sample carefully in the centre of an adapter. The efficiency calibrations were carried out using Geometry composer. Initially, the homogeneity was determined by calculating the relative standard deviation of the Co-60 and Cs-137 results. As the RSD% were 0.9 and 1.1%, respectively, the samples were considered to be homogenous.

Stability of the resin sample was discussed in the kick-off meeting as unknown amount of moisture was present in the samples. Therefore, the samples were double bagged in order to keep the moisture level as stable as possible during transport. Participants agreed to monitor the weight fluctuation of the samples during storage.

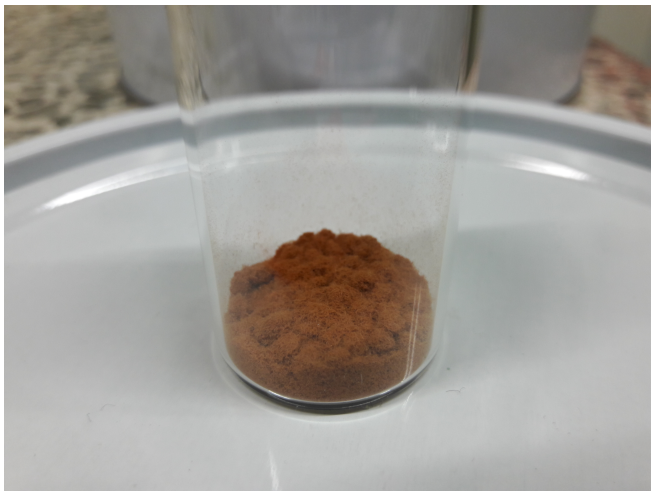

Figure 1. Example of a studied spent ion exchange resin sample in a liquid scintillation vial (0.8 g)

The homogeneities were additionally assessed using Equation 1 according to the ISO13528 standard after the submission of participants' results. Between-sample standard deviation, s_s was calculated from sample averages, between-test-portion ranges, general average, standard deviation of sample averages, within-sample deviation and between-sample standard deviation. The Equation 1 was true when the robust standard deviation of participant results were used as σ_{pt} (see chapter 9.4). The results showed that the samples were homogenous also according to the ISO standard.

$$s_s \leq 0.3\sigma_{pt} \quad (1)$$

Where
s_s= between-sample standard deviation
σ_{pt} = robust standard deviation of participant results

4. Radiochemical analysis

Participants carried out the radiochemical analyses based on either internal or published procedures [l'Annunziata 2012; Baudat 2021 Gautier et al, 2015, 2020; Hazan et al. 1965; Hou et al., 2005a, 2005b, 2007, 2016; Lee et al. 2007, 2011, 2016; Leskinen et al., 2020a; Passo et al. 1994; Triskem international method 2001, 2003a, 2003b, 2014; Shi et al., 2012]. The procedures had similar components, which are summarised in following sections.

The pre-treatment and acid digestion methods are listed in Table 2. Pre-treatment of the sample was carried out (drying/ashing) by two partners prior to acid digestion. Radiochemical analyses of non-volatile DTMs and Tc-99 began with decomposition of the solid matrix which was carried out using different acid mixtures on a hot plate, heating mantle or in a microwave oven. The carriers (i.e. Sr, Fe, Ni, Re as Tc surrogate) or radioactive standards (Ni-63, Tc-99m, Sr-85) were added by all partners whereas hold back carriers (e.g. Cr, Mn, Cs, Sb, Nb, Zr, Mo, Cd, Eu, Y and Co) were added by five partners.

Table 2. Acid digestion methods for spent ion exchange resins

Sample #	Pre-treatment	Acid digestion		Carriers and tracers*
		Heating	Acid mixture	
1	Dried	micro wave oven	conc. HNO_3	Fe-55, Ni-63 analysis: Ni and Ni-63
2	No	hot plate	conc. H_2SO_4 and later conc. HNO_3 added	Sr-90, Fe-55, Ni-63 analysis: Sr, Fe, Ni
3	No	hot plate	conc. H_2SO_4:HNO_3:$HClO_4$ Tc-99 with 8M HNO_3	Sr-90, Ni-63, Fe-55 analysis: Sr, Ni, Fe Tc-99 analysis: Re
4	No for volatile DTM. Dried at 150 °C first, then ashed at 500 °C	hot plate	conc. HNO_3:HCl:H_2O_2	Fe-55, Ni-63, Sr-90 analysis: Fe, Ni, Sr
5	No	micro wave oven	conc. HNO_3	Sr-90 analysis: Sr and Sr-85 Fe-55, Ni-63 analysis: Fe, Ni, Cr, Mn, Cs, Sb, Nb, Zr, Mo, Cd, Eu, Co
6	No	hot plate	conc. H_2SO_4:HNO_3:$HClO_4$	Fe-55, Ni-63 analysis: Ni, Fe, Co, Sr, Eu, Mn, Cs
7	No	micro wave oven	conc. HNO_3:HCl	Sr-90 analysis: Sr, Ni-63 analysis: Fe, Ni, Co, Fe-55 analysis: Fe, Ni, Co, Ag, Cs
8	No	heating mantle	conc. HNO_3:HCl:H_2O_2	Fe-55, Ni-63, Sr-90, Tc-99 analysis: Fe, Ni, Sr, Co, Eu, Cs, Mn, Sb, Ca, Tc-99m
9	No	micro wave oven	conc. HNO_3	Fe-55, Ni-63, Sr-90, analysis: Fe, Co, Ni, Sr, Y

*Carriers refer to carriers and hold-back carriers. Radioactive tracers and carriers were used for measurement of yields.

4.1. Radiochemical analysis of Sr-90, Fe-55, Ni-63 and Tc-99

Table 3 summarises the overview of Sr-90, Fe-55, Ni-63 and Tc-99 separation (i.e., separation of the RN from other RNs of interest) and purification (i.e., purification from interfering RNs) methods. In general, three out of nine partners carried out initial evaporation of the acid digested solutions. Separations of Fe-55, Ni-63 and Sr-90 from each other were carried out either using

precipitations (i.e. chloride, hydroxide and carbonate) and/or resin treatments (i.e., TRU, AG or DOWEX resins). Sr purification was mainly carried out using Sr or SrSpec resin, but also with sequential precipitations (sample #7). Sr resin treatment was carried out directly after acid digestion for samples #4 and #5. Majority of the partners used Ni resin for purification of Ni-63 fraction while one used DMG precipitation (sample #4). Tc-99 was purified either from the same acid digested sample for Fe and Ni analysis (sample #8) or from a separate acid digestion sample (#3). Tc sample #8 was purified from the supernatant of sequential Fe, Ni and Sr precipitations using anion exchange and TEVA resins. Tc sample #3 was purified from interfering RNs using AG resin.

Purified Sr-90 fractions were measured mainly after ingrowth of Y-90 using Cerenkov LSC (#2, #4, #8) or LSC (#3, #7), but also proportional counter was used for sample #7 analysis, Risø beta counter for sample #5, and ICP-MS for Sample #9. Sample #5 analytical method was different compared to the other methods, as the purified fraction was further treated before proportional counter measurement. The purified Sr fraction was first settled for two-three weeks and the ingrown Y-90 was removed from the solution by hydroxide precipitation using NH_3 to adjust pH 8. Sample was filtered and precipitate discarded. Saturated oxalic acid was added into the supernatant and Sr precipitated at pH 3 using NH_3. Sr was filtered on a filter and the sample was measured using the beta counter. The filter was ashed after beta counting and the Y yield was determined using EDTA titration.

All purified Fe-55 and Ni-63 fractions were measured using LSC. Yields were determined mainly with stable Fe and Ni analyses (#2-#8). In case of sample #1, Fe yield was estimated and Ni yield was determined using Ni-63 standard addition.

Sr, Fe and Ni yields were determined gravimetrically (#7 Sr fraction), stable Sr analysis (#2, #3, #4, #7, #8, #9) or measurement of a radioactive tracer (#5) were implemented for yield determination.

The purified Tc-99 fractions were measured using LSC. Chemical yield of Tc-99 in sample # 3 yield was determined using stable Re (Tc surrogate) analysis and sample #8 yield was using Tc-99m gamma spectrometry.

Table 3. Separation and purification of Sr-90, Fe-55, Ni-63 and Tc-99

Sample #	**RN**	**Evapo-ration**	**Separation using precipitation**	**Separation using a resin treatment**	**Purification from interfering RNs**	**Measurement**
1	Fe-55	Evaporated to dryness	AgCl (addition of $AgNO_3$) for possible Ag removal	Supernatant through TRU resin: Fe retained, Ni through	-	Yield with Ni-63 standard addition, Fe estimated 90% Measured by LSC
	Ni-63				Ni resin	
2	Sr-90	-	Hydroxide precipitation: Sr in supernatant, Fe, Ni in precipitate	-	Sr resin	Yield with MP-AES. Activity with LSC after ingrowth of Y-90
	Fe-55				Dowex	

	Ni-63			Dowex: Fe retained, Ni through	Ni resin	Yield with MP-AES. Measured by LSC
3	Sr-90	Evaporated to near dryness	-	AG resin: Fe retained, Ni and Sr through	Sr resin: Sr retained, Ni through	Yield with ICP-OES. Activity with LSC after ingrowth of Y-90
	Fe-55				-	Yield with ICP-OES. Activity with LSC
	Ni-63				Ni resin	
	Tc-99	Evaporated carefully to near dryness	-	-	AG resin	Yield with ICP-OES (Re surrogate). Activity with LSC
4	Sr-90	-	-	-	SrSpec resin	Yield with ICP-OES. Activity with Cherenkov LSC after ingrowth of Y-90
	Fe-55		Fe, Ni hydroxide precipitation using NaOH	Fe, Ni separated with hydroxide precipitate treatment with conc, NH_4OH	Dowex	Yield with ICP-OES. Activity with LSC
	Ni-63				DMG precipitation	
5	Sr-90	-	-	-	Sr resin	Yield with Sr-85 gamma spectrometry and EDTA titration. Activity measured with beta counter.
	Fe-55	conc. HCl added and evaporated to dryness	AgCl (removed) and Fe, Ni hydroxide precipitation (addition of NaOH)	AG resin: Fe retained, Ni through	AG resin	Yield with ICP-OES. Activity with LSC.
	Ni-63				Ni resin	
6	Fe-55	-	NaOH precipitation for Fe, Ni	AG resin: Fe retained, Ni through	Fe resin	Yield with ICP-MS. Activity with LSC.
	Ni-63				Ni resin	
7	Sr-90	Evaporated to dryness	Sequential precipitation using HNO3	-	-	Gravimetry with proportional counter

			(fuming or conc.), ammonia and oxalate			or ICP-OES with LSC.
	Sr-90		-	TRU resin	Sr resin	
	Fe-55		Ammonia	AG resin Fe retained, Ni through	TRU resin	ICP-OES with LSC
	Ni-63		-	AG resin Fe retained, Ni through	Ni resin	
8	Sr-90	-	Sequential hydroxide precipitation for Fe and Ni and $SrCO_3$-$CaCO_3$ precipitation for Sr	-	Sr resin	Yield with ICP-OES. Activity with Cherenkov LSC after ingrowth of Y-90
	Fe-55			AG resin; Fe retained, Ni through	-	Yield with ICP-OES. Activity with LSC.
	Ni-63				Ni resin	
	Tc-99			-	Anion exchange TEVA resin	Yield with Tc-99m gamma spectrometry. Activity with LSC.
9	Fe-55	-	Fe and Y precipitated with ammonia	-	AG resin (twice)	Yield with ICP-MS. Activity with LSC.
	Sr-90			SrSpec resin	-	Yield with ICP-MS. Activity with LSC and ICP-MS
	Ni-63				AG resin	No analysis result

4.2. Radiochemical analysis of H-3 and C-14

Table 4 summarises the overview of H-3 and C-14 analyses. The H-3 analyses were carried out using thermal oxidation (#3, #7) and alkaline distillation (#4). Thermal oxidation was carried out using a pyrolyser (Raddec or Eraly), in which the sample is subjected to increasing temperature. Temperature was gradually increased to 900 °C (sample #3) or 950 °C (sample #7) and released H-3 was collected using 0.1 M HNO_3 (#3) and 0.2 M HCl (#7). Yields were determined experimentally using H-3 spiked resin (#3) and representative oil sample (#7). In alkaline distillation, the sample #4 was first distilled with KOH, KMnO4 and deionised water. H-3 was recovered from a specific fraction of the distillate. The C-14 analyses were carried out either together with H-3 analysis using thermal oxidation (#3, #7) or wet oxidation acid stripping, in which the sample was treated with $K_2S_2O_8$, $AgNO_3$ and H_2SO_4 and 96 °C heating for 3 h. In all cases, the released C-14 as CO_2 was collected in Carbo-Sorb.

Table 4. Determination of H-3 and C-14

Sample #	RN	Treatment	Yield	Measurement
3	H-3	Thermal oxidation	Spiked inactive resin	LSC
	C-14			
4	H-3	Alkaline distillation	Spiked inactive resin	LSC
	C-14	Wet oxidation acid stripping		
7	H-3	Thermal oxidation	Reference oil	LSC
	C-14			

5. Analysis of gamma emitters

All partners carried out the gamma-emitter analyses. Measurement conditions, sample information, efficiency calibration and coincidence correction information are presented in Table 5. The gammaspectrometric analyses were carried out mainly with samples in solid form, but also in acid digested solutions. All laboratories used HPGe detectors placing the sample on top of the endcap at a specified distance. Low dead time was achieved with longer distance. Efficiency calibrations were carried out using calibration solutions (standard geometry), LabSOCS, ISOCS, Eu-152 source, point source, Monte Carlo efficiency transfer method with multi radionuclide source and dual polynomial fitting.

Table 5. Gamma spectrometric measurements

ID #	Measurement conditions			Sample information	Efficiency calibration	Coincidence correction
	Distance (cm)	Dead time (%)	Measure-ment time (s)			
1	0	3.15	-	Acid digested 0.1546 g diluted to 100 ml, 50 ml aliquot measured	LabSOCS and standard geometry	Yes
	0	3.45	-			
2	12	2	3605	Original solid sample	Dual polynomial fitting	No (long distance)
3	20	1	247700	Original solid sample	ISOCS	Yes, but not significant due to large distance
4	5	2.47	7200	Acid digested 0.4068 g	Eu-152 standard	No
	11	2.82	7200	Original solid sample		
5	10	4.28	73621	Original solid sample	Standard geometry	EFTRAN
6	0	1.13	3600	Original solid sample	Standard geometry	-
7	15	0.2	86400	Solid 0.08 g	Mathematical calibration (LabSOCS)	No
	0.7	2	10800	Liquid 0.08 g	Standard geometry	Yes

8	5	-	72000	Original sample transferred into 20 ml LSC	Monte Carlo efficiency transfer method and multi RN source.	Yes with Monte Carlo Code
9	0	7	5000 and 25 000	Acid digested samples (3 solutions with ~0,1 g of resin each)	Standard geometry	No (direct comparison with the calibration radionuclides

6. Methodology for statistical analysis of the reported results

The statistical analyses of the submitted results were carried out using the ISO 13528 standard similarly to DTM Decom projects I-II [1,3]. Since the original RN activity concentrations were not known, a robust statistical method was utilised for calculation of assigned values based on the participants's results. Robust mean and robust standard deviation were calculated using Algorithm A. Algorithm A is robust for outliers, when the expected proportion of outliers is less than 20%. Performance assessment was carried out using z score (Eq. 2), which is the recommended method in this case type of exercise. The analysis results with z score were acceptable when $|z| \leq 2.0$, a warning signal was given for results with $2.0 < |z| < 3.0$, and results were unacceptable when $|z| \geq 3.0$.

$$z_i = (x_i - x_{pt}) / \sigma_{pt} \quad (2)$$

Where
x_{pt} = the assigned value
σ_{pt}= standard deviation for the proficiency assessment

7. Preliminary results

The preliminary meeting was held to discuss the radioanalytical procedures and reported results. As seen in Figure 2, the result presented in graphs without scale to demonstrate trends and not on individual results. The Fe-55 results show a general, agreeable trend. However, sample #6 has a noticeable variation in the replicates and additionally also significantly large uncertainties, which were in fact, caused by difficulties in the uncertainty calculations. Additionally, sample #4 deviates from the other results to some extent. The possible reason was suggested to be caused by luminescence or an error in yield measurement. The Ni-63 results also show a general, agreeable trend whereas significant deviation of sample #4 from the general trend and to some extend also #6. Reasons for the deviation of #4 were suggested to originate in Co-60 contamination in the sample (higher than average result). Smaller number of Sr-90 analyses were carried out, but the submitted results show an agreeable trend without clear deviations. The H-3 results showed that samples #3 and #7 results were below the detections limits whereas one result (#4) was above the detection limit. The samples #3 and #7 were analysed using thermal oxidation whereas #4 was analysed using alkaline distillation. The C-14 results showed good consistency between two out of three results i.e., #3 and #7 which both were analysed using thermal oxidation. Sample #4 deviated from the other results. However, not enough data entries were submitted for clearer trend analysis. The Tc-99 results suffered

from lack of data entries. One result was below the detection limit and only one result above the detection limit.

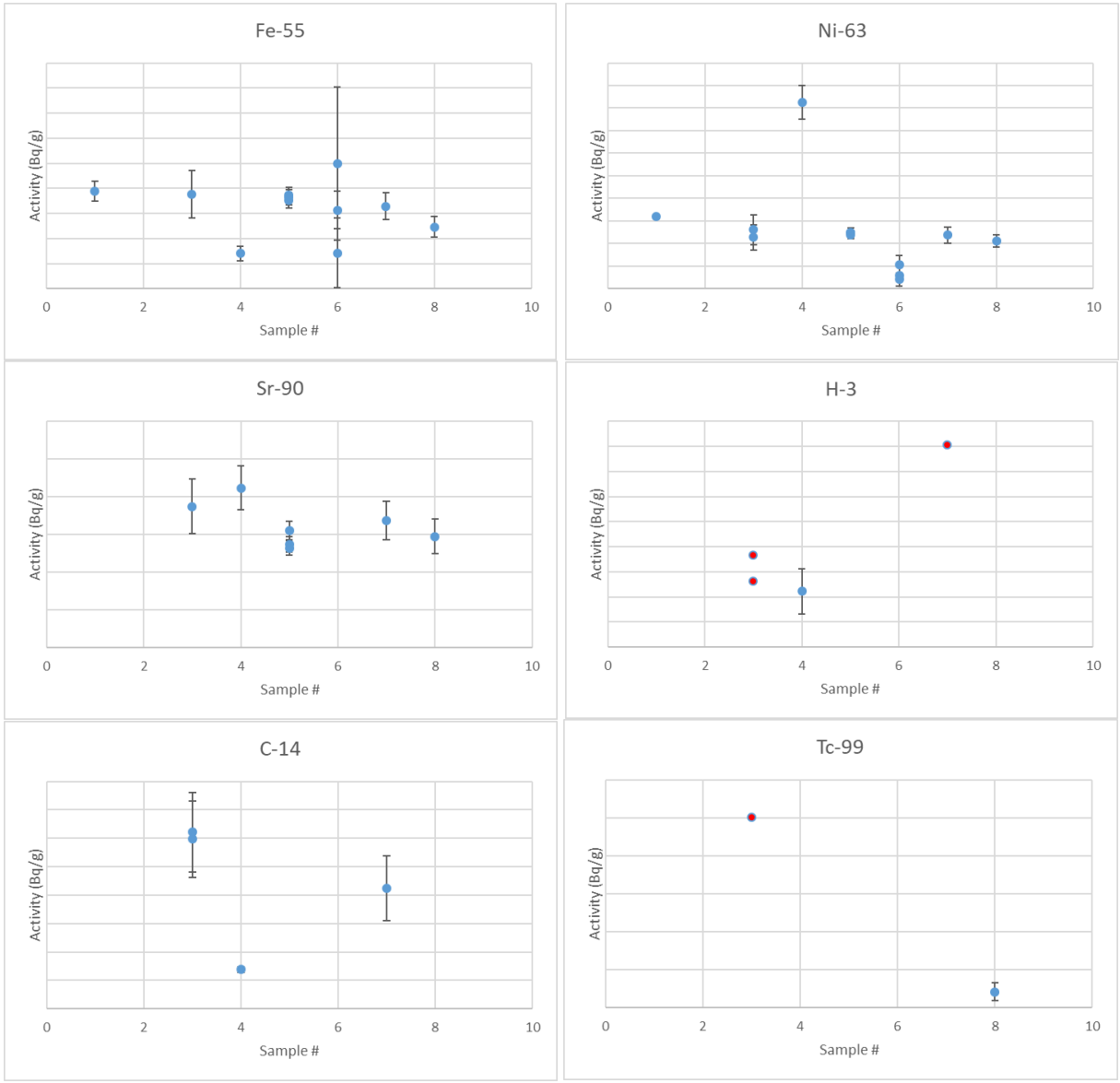

Figure 2. Preliminary DTM results in spent ion exchange resin with 2k uncertainties.

Figure 3 shows the preliminary gamma-emitter results submitted prior to the preliminary meeting. The results show that general trends can be seen for Mn-54, Co-60, Cs-134 and Cs-137 showing good consistency between samples #3 to #8 whereas #1 and #2 are slightly higher than the overall trend. Smaller amount of entries were submitted for Co-57, Co-58 and Sb-125, whose activity concentrations were low. It was concluded that all laboratories will submit limit of detections for the final meeting. Table 6 shows additional gamma emitters which were submitted by one or two laboratory, namely Be-7, Cd-109, Nb-95, Ag-110m, Eu-152 and Th-231. Discussions in the preliminary meeting suggested that at least Be-7, Cd-109, Eu-152 and Th-231 are most likely false positives and they should be re-checked.

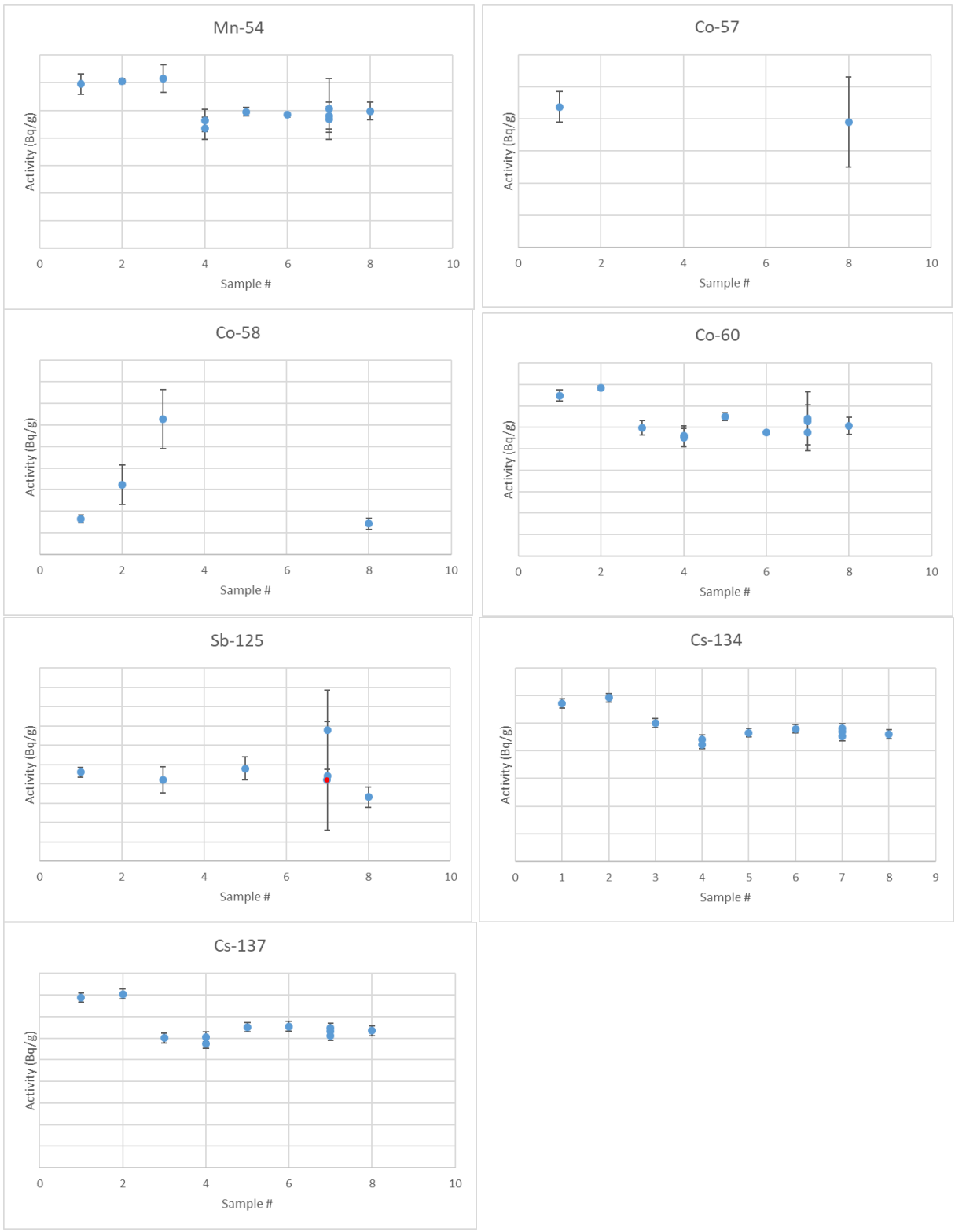

Figure 3. Preliminary results for gamma-emitters in spent ion exchange resin sample with 2k uncertainties.

Table 6. Preliminary gamma spectrometric identifications of radionuclides by one or two participants in the spent resin

Sample #	Be-7	Cd-109	Nb-95	Ag-110m	Eu-152	Th-231
2	x	x				
3			x	x		
5					x	
6		x				x

8. Final results and statistical analysis

The final meeting was held to present and discuss the final results. Updated results are indicated in the text. Assigned values were calculated from the results which were submitted before the deadline. Additionally, sample #9 results were submitted after the final meeting and they were not included in the assigned values calculations nor presented in Figures 4-8, which were presented in the final meeting.

8.1. Stability of the sample during storage

The weight fluctuations normalised to the initial weights of the samples are presented in Figure 4. The results show that the samples were stable during storage. No difference is seen between the samples kept in room temperature and fridge. One partner reported a moisture percentage of 0.6 %. Therefore, the analysed with or without the heat pre-treatment were considered not to affect the results.

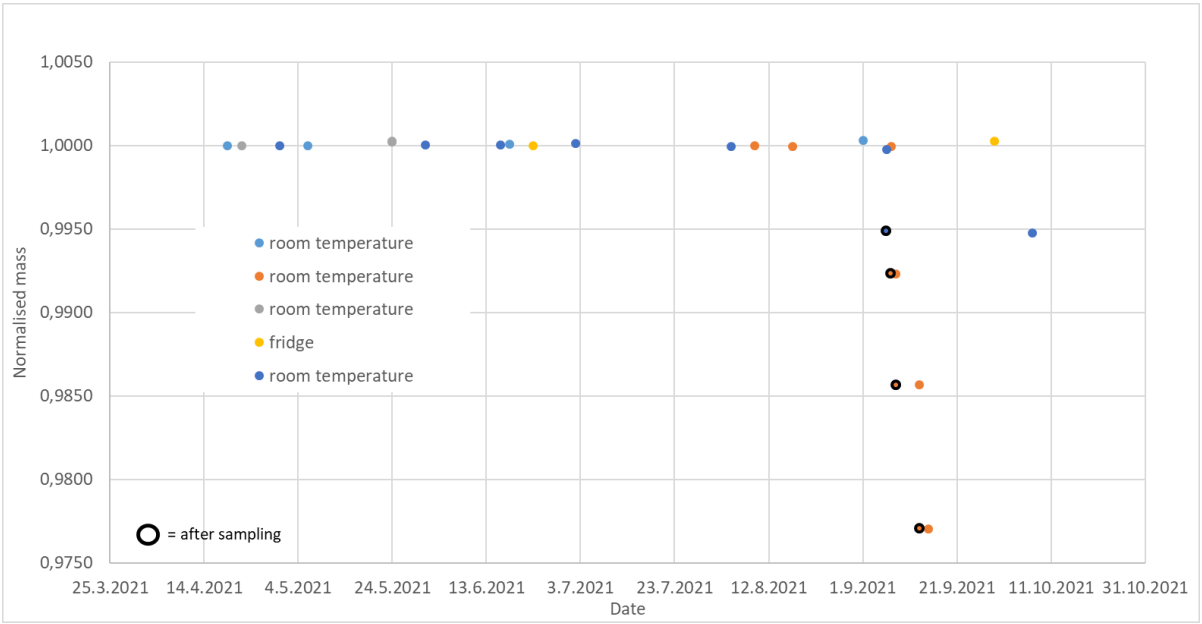

Figure 4. Stability of the studied spent ion exchange resin samples during storage in room temperature and fridge.

8.2. Original chemical compositions of the sample

Four laboratories analysed stable Fe, Ni and Sr concentrations in the spent ion exchange resin after acid digestion. The results in Table 7 show good consistency for Fe results in samples #4,

5 and 7 whereas #3 is approximately half of the value reported by others. Sample #3 original Fe content calculations were re-checked for the final meeting and no calculation error was found. Sample #4 measurements and calculations were also re-checked for the final meeting as one of the reasons for Fe-55 and Ni-63 result deviations from general trend was suggested to originate from yield (consequently original composition) calculations.

Table 7.Analytical results of Fe, Ni and Sr concentrations in the spent ion exchange resin

Sample #	Digested mass (g)	Fe (mg/g) ± 2k	Ni (mg/g) ± 2k	Sr (mg/g) ± 2k
3	0.039*	13.4±1.1	<LOD	<LOD
4	0.0061	-	-	<0.004
	0.0203*	34.8±0.7	<0.098	-
5	0.0751±0.86	31.87±0.86	<0.52	-
7	0.13	34.0±6.8	0.247±0.0494	<0.0107

*re-checked for the final meeting

8.3. DTM results and statistical analysis

The measured and estimated yields of Fe-55, Ni-63, Sr-90 and Tc-99 analyses are shown in Table 8. In general, the Sr, Fe, Ni, Tc yields are between 60-90% whereas extreme yields (i.e. 26% and 183%) were reported indicating significant difficulties in the yield measurement or calculations. H-3 yields were between 89-100% and C-14 between 74-100%.

Table 8. Yields of Fe-55, Ni-63, Sr-90 and Tc-99 analysis results.

Sample #	Yield (%)					
	Fe-55	Ni-63	Sr-90	Tc-99	H-3	C-14
1	90 (estimated)	80-87	-	-	-	-
2	65 (estimated)	99	55 (estimated)	-	-	-
3	100	76	65	60	90	100
4	58	61	54	-	89	83
5	94-96	86-93	97-101	-	-	-
6	59-183	26-105	-	-	-	-
7	95	90	71 (proportional counter) 97 (LSC)	-	100	74
8	95	91	95	94	-	-
9	56-69	-	100	-	-	-

The final meeting H-3, C-14, Fe-55, Ni-63, Sr-90 and Tc-99 analysis results with replicates are shown in Figure 5. The H-3 results show that #3 and #7 results were below limits of detection results (marked with red dot). The only result above limit of detection was submitted for sample #4, which was analysed using alkaline distillation whereas below limit of detection results were obtained with thermal oxidation. The C-14 result range is between 1400 and 6000 Bq/g. Samples #3 and 7 were carried out with thermal oxidation whereas sample #4 was analysed using wet oxidation acid stripping. Further analyses should be carried out for conclusive results. Fe-55 and Ni-63 analysis results for sample #2 were new data entries whereas the sample #4

results were re-checked after preliminary meeting. The corrected #4 results show excellent alignment with the overall trends. No re-calculations after preliminary meeting were utilised for #6 Fe-55 and Ni-63 results. Sample #2 Sr-90 result was also a new data entry after the preliminary result showing significant deviation from the overall trend. The partner was notified for the difference, but no obvious blunders were found in calculations. No new data entries were submitted for Tc-99 analysis. However, the Tc-99 results show that #3 result limit of detection was 2.5 Bq/g whereas sample #8 activity was measured to be 0.21 Bq/g.

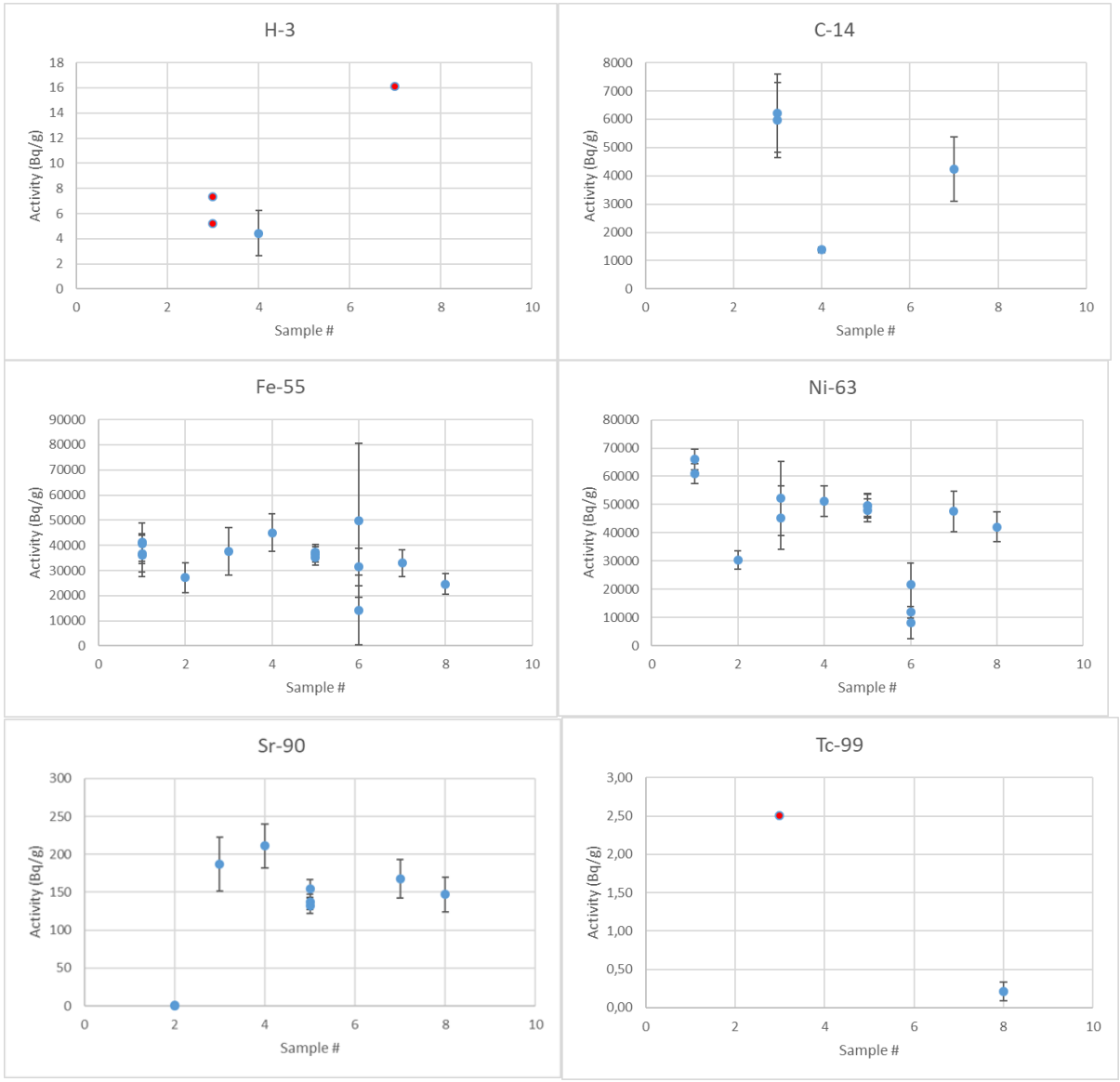

Figure 5. The final H-3, C-14, Fe-55, Ni-63, Sr-90, Tc-99 results with 2k uncertainties in spent ion exchange resin samples. Red color indicates limit of detection.

Statistical analysis was carried out for Fe-55, Ni-63 and Sr-90 results as large enough number of analyses were carried out. Each partner had one data entry per analysis. Table 9 shows the statistical analysis results i.e., number of data entries, number of iterations, assigned values and robust standard deviations. Figure 6 summarises the data entries and calculated assigned value with 2k uncertainties. Table 10 shows the z score results.

The statistical analysis of Fe-55 results were carried out using 8 data entries and 4 iterations. The assigned value for the Fe-55 activity concentration was calculated to be 34.3 ± 14.9 kBq/g (2k). The robust standard deviation of the assigned value was 21.8%. Comparison of Figure 6 and Table 10 for Fe-55 results highlight how all the results are located in the acceptable range of z score (i.e., below 2).

The statistical analysis of Ni-63 results were carried out using 6 data entries and 8 iterations. The assigned value for the Ni-63 activity concentration was calculated to be 50.9 ± 8.2 kBq/g (2k). The robust standard deviation of the assigned value was 15.8%. Comparison of Figure 6 and Table 10 for Ni-63 results show that even though sample #1 z score is within the acceptable range (i.e., below 2), it is above the uncertainty of the assigned value. Sample #3 Ni-63 z score 2.6 is in warning range (i.e., between 2 and 3) and sample #6 z score 4.6 is in unacceptable range (i.e., above 3).

The statistical analysis of Sr-90 results were carried out using 5 data entries and 2 iterations. The assigned value for the Sr-90 activity concentration was calculated to be 171.2 ±36.0 Bq/g (2k). The robust standard deviation of the assigned value was 18.8%. Comparison of Figure 6 and Table 10 for Sr-90 results show that all results are in acceptable range except sample #2 result, which is clearly in unacceptable range (i.e., above 3).

Table 9. Sample numbers and z scores of Fe-55, Ni-63 and Sr-90.

	Fe-55	**Ni-63**	**Sr-90**
Number of data entries in calculations	8	6 (#2 and #6 outliers)	5 (#2 outlier)
Number of iterations	4	8	2
Assigned value	34.3±14.9 kBq/g	50.9±8.2 kBq/g	171.2±36.0 Bq/g
Robust standard deviation (%)	21.8	15.8	18.8

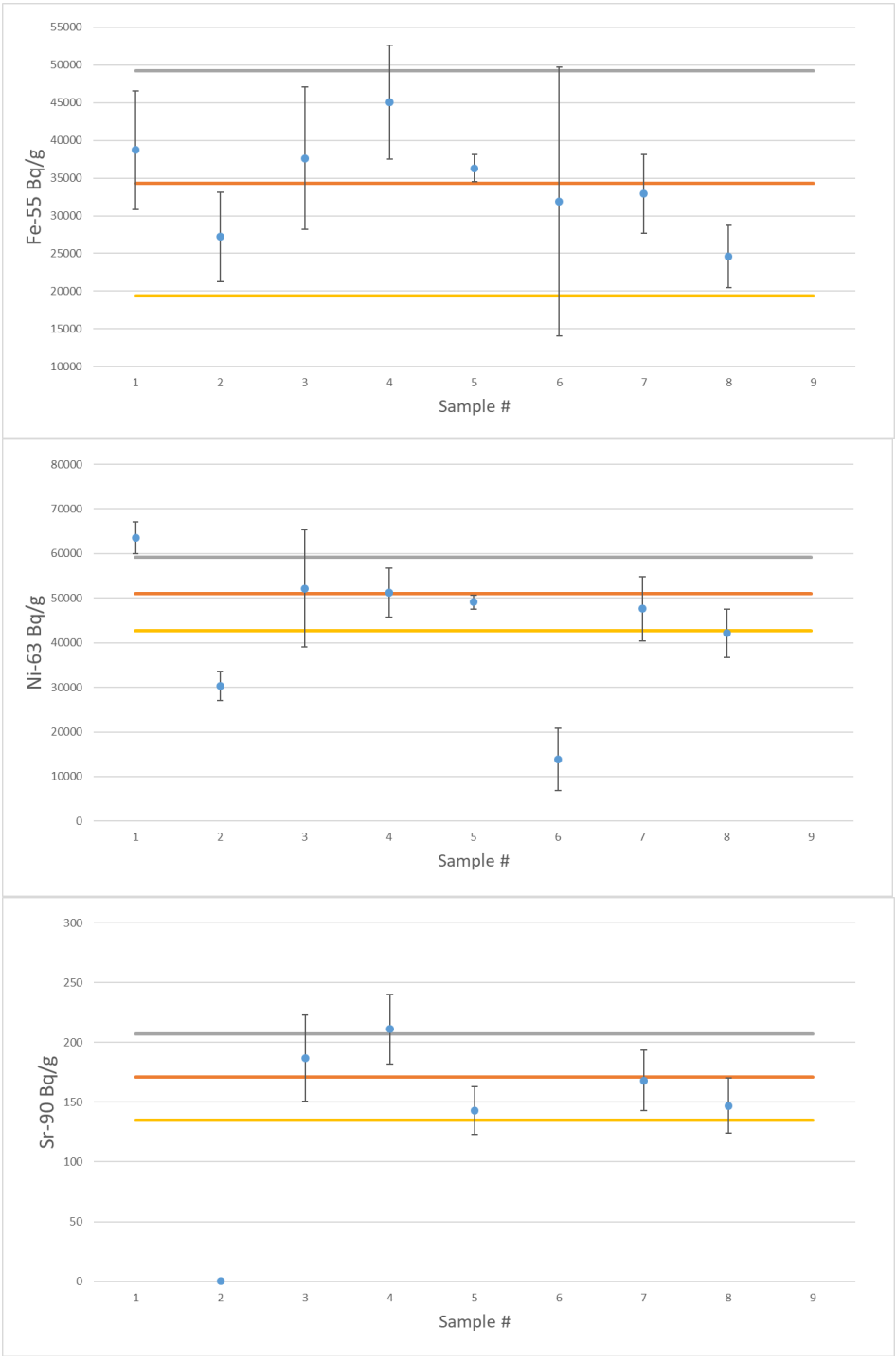

Figure 6. The final Fe-55, Ni-63 and Sr-90 results in spent resin samples and assigned value with 2k uncertainties.

Table 10. Sample numbers and z scores of Fe-55, Ni-63 and Sr-90.

Sample #	**z score**		
	Fe-55	**Ni-63**	**Sr-90**
1	0.6	1.6	-
2	0.9	2.6	5.3
3	0.4	0.2	0.5
4	1.4	0.0	1.2
5	0.3	0.2	0.9
6	0.3	4.6	-
7	0.2	0.4	0.1
8	1.3	1.1	0.8
9	0.2	-	0.1

8.4. Gamma emitter final results and statistical analysis

The final meeting gamma analysis results with replicates and activity concentrations are shown in Figure 7. The overall Mn-54, Co-60, Cs-134 and Cs-137 results show a similar trend i.e, samples #1 and #2 are little bit above and #3 and #4 little bit below all the rest of the results. Above the limit of detection results for Co-57 were approximately 50 Bq/g whereas samples #4 and #7 were measured mainly in liquid form or smaller sample amount. Co-58 results show a general trend around 300-400 Bq/g whereas two samples measured in liquid form were below the limit of detection (# 4 and #7). Sb-125 results show a trend as mentioned above i.e., measurements in liquid form (lower amount of resin) yielded results below detection limits.

Revision of Table 6 resulted in allocation of all the results as false positives attributable to gamma-rays commonly found in background spectra , as well as X-rays from lead.

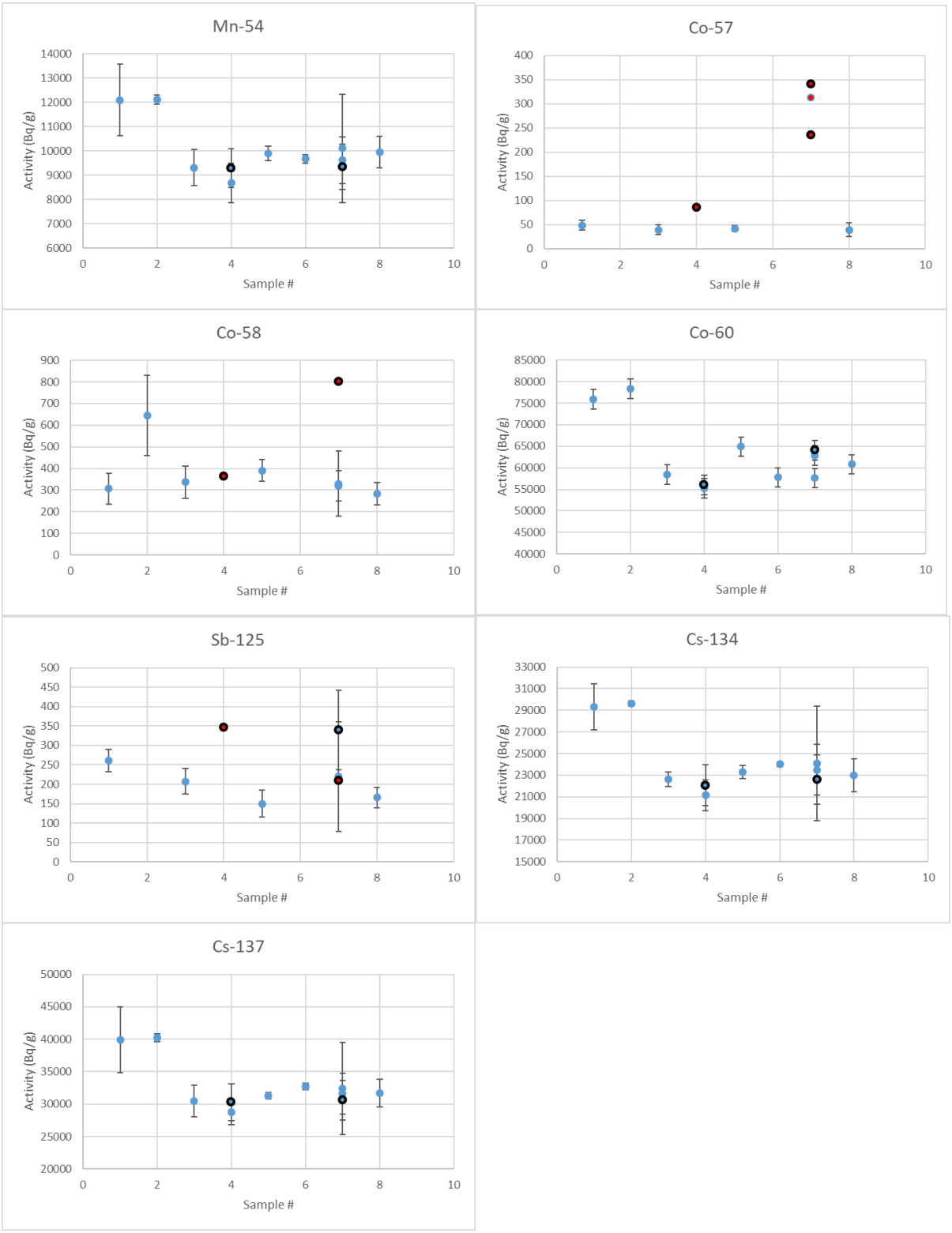

Figure 7. Gamma-activity results in spent ion exchange resin samples with 2k uncertainties. Red color indicates limit of detection, bold circle measurement in liquid form.

Statistical analysis of the gamma emitter results above the limit of detection with one data entry per analysis per partner are shown in Table 11. Figure 8 summarises the data entries and calculated assigned value with 2k uncertainties. Table 12 shows the z score results. Comparison of the Figure 8 and Table 12 results show that only sample #2 Co-58 result is in unacceptable

range whereas all the other results are in acceptable range and within the uncertainties of the assigned values.

Table 11. Number of samples, assigned activity values and robust standard deviations gamma-emitters.

Radionuclide	Number of data entries in calculations	Number of iterations	Assigned value ± robust standard deviation [kBq/g]	Robust standard deviation (%)
Mn-54	8	7	10.2±2.8	13.6
Co-57	4	3	0.041±0.006	6.9
Co-58	6	7	0.354±0.132	18.6
Co-60	8	7	64.2±19.1	14.9
Sb-125	5	3	0.195±0.045	20.6
Cs-134	8	10	24.6±6.9	14.0
Cs-137	8	10	33.4±9.6	14.4

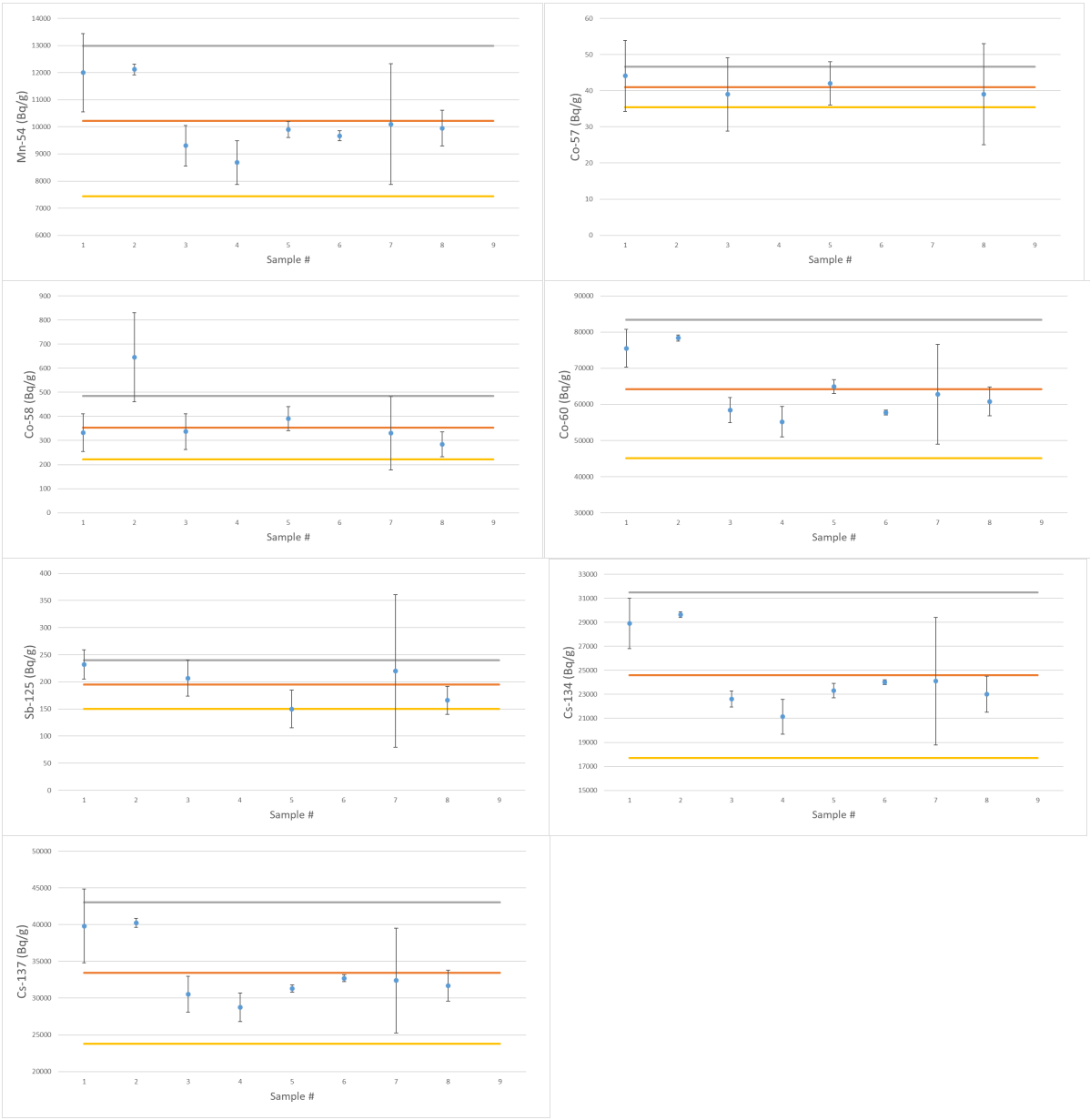

Figure 8. Revised activities of gamma-emitters in spent ion exchange resin with 2k uncertainties.

Table 12. Sample numbers and z scores of gamma-emitters.

Sample #	**z score**						
	Mn-54	**Co-57**	**Co-58**	**Co-60**	**Sb-125**	**Cs-134**	**Cs-137**
1	1.3	1.1	0.3	1.2	0.9	1.3	1.3
2	1.4	-	4.4	1.5	-	1.5	1.4
3	0.7	0.7	0.3	0.6	0.3	0.6	0.6
4	1.1	-	-	0.9	-	1.0	1.0
5	0.2	0.3	0.5	0.1	1.1	0.4	0.4
6	0.4	-	-	0.7	-	0.2	0.1
7	0.1	-	0.4	0.1	0.6	0.1	0.2
8	0.2	0.7	1.1	0.4	0.7	0.5	0.4
9	0.8	-	-	0.6	-	1.5	0.8

9. Summary

DTM and gamma-emitter analyses were carried out for the spent ion exchange resin sample. The focus was on Fe-55, Ni-63, Sr-90 and gamma emitter analysis whereas H-3, C-14 and Tc-99 were optionally analysed. The results were analysed according to the ISO 13528 standard when applicable. The assigned value, to which results were compared, was calculated from participants's results. The performance was assessed using z score which indicates result's deviance from the assigned value.

The acid digestions with different mixtures of acids were able to completely dissolve the matrix. The yields were generally good. The Fe-55 assigned value calculated from the partners' results was 34.3±14.9 kBq/g (2k). The robust standard deviation was 21.8% indicating some scattering of the results without clear extremes. All z scores were in acceptable range. The Ni-63 assigned value was 50.9±8.2 kBq/g (2k) with 15.8% robust standard deviation. The results showed a clear trend with one submitted value deviating the overall trend (z>3) and two in some extent (z score with warning signal). The Sr-90 assigned value was 171.2±36.0 kBq/g (2k) with 18.8% robust standard deviation. The results showed a quite clear trend with one submitted value deviating the overall trend (z>3). Low number of results (2-3) were submitted for the H-3, C-14 and Tc-99 analyses and statistical analyses were not carried out.

All partners submitted activity results for Mn-54, Co-60, Cs-134 and Cs-137 gamma-emitters, whose activities were between 10-64 kBq/g. Co-57, Co-58 and Sb-125 activities were between 41-354 Bq/g. Some partners either did not submit results for the latter radionuclides, or the activities were below limits of detection mainly due to the measurement of acid digested subsamples. The z scores were all except one in the acceptable range.

As a conclusion, the DTM Decom I-III projects have increased the capabilities in DTM determinations. Beneficial discussions have been carried out during the projects and collective information sharing was carried out throughout the three years. Similarly to DTM Decom I and II projects, DTM Decom III project produced interesting set of results and they will be further analysed and discussed in a peer reviewed publication together with modelling results. Analysis of alpha emitters in the same resin will be carried out in RESINA project.

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Key words Decommissioning, Difficult-to-measure radionuclides, intercomparison exercise, spent ion exchange resin