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Determination of ^{63}Ni and ^{59}Ni in spent ion-exchange resin and activated charcoal from the IEA-R1 nuclear research reactor

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HIGHLIGHTS

- A radiochemical method was adapted for determination of ^{59}Ni and ^{63}Ni.
- ^{59}Ni and ^{63}Ni were determined in samples of radioactive wastes from research reactor.
- The activity concentration of ^{59}Ni was measured by X-ray spectrometry.
- The activity concentration of ^{63}Ni was measured by liquid scintillation counting.
- Average ratio of measured activity concentrations of ^{63}Ni and ^{59}Ni agrees with theory.

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ABSTRACT

A radiochemical method has been adapted to determine ^{59}Ni and ^{63}Ni in samples of radioactive wastes from the water cleanup system of the IEA-R1 nuclear research reactor. The process includes extraction chromatographic resin with dimethylglyoxime (DMG) as a functional group. Activity concentrations of ^{59}Ni and ^{63}Ni were measured, respectively, by X-ray spectrometry and liquid scintillation counting, whereas the chemical yield was determined by ICP-OES. The average ratio of measured activity concentrations of ^{63}Ni and ^{59}Ni agree well with theory.

1. Introduction

The IEA-R1 is a 5 MW pool-type nuclear research reactor moderated and cooled by light water. It is located at the Nuclear and Energy Research Institute (IPEN/CNEN-SP) and used for scientific research as well as to produce radioisotopes (Vasconcellos and Saiki, 2006; Vasconcellos et al., 2004). Currently, the core of the IEA-R1 nuclear research reactor employs 24 plate-type elements usually designated as Material Testing Reactor (MTR) fuel elements (Terremoto et al., 2000; Mora et al., 2011), as well as 4 fork-type control rods of silver–indium–cadmium alloy (Ag–In–Cd alloy in proportion of 80%, 15%, 5%, respectively) with a thin cladding of metallic Ni.

Nuclear reactions in the reactor generate radioactive isotopes of Ni as activation products, mostly when thermal neutrons impinge on the cladding of the control rods, although neutron activation of a few stainless steel structural components also contributes to generate these radionuclides.

Such activation products are released by corrosion and carried along with the cooling water to the cartridge filters, activated charcoal beds and ion-exchange resin beds that constitute the water cleanup system of the reactor. When the purification capability of these materials is exhausted, they are replaced and become low-level radioactive waste. Their radioactive inventory must be determined as a first and fundamental management step.

For radioactive waste characterization, the relevant Ni isotopes are ^{59}Ni and ^{63}Ni, whose properties are summarized in Table 1.

These Ni isotopes are included among the difficult to measure (DTM) radionuclides (IAEA, 2009) because of their long half-life and radioactive decay with no emission of gamma-rays. As a consequence, quantitative and selective separation of ^{59}Ni and

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Table 1
Properties of the relevant Ni isotopes regarding radioactive waste characterization: half-life $T_{1/2}$, main production nuclear reactions, threshold energy E_{th} of the nuclear reaction, isotopic abundance f of the stable target nucleus, radioactive decay mode (EC–electron capture; β^-–emission of beta particle) and main radiations emitted in the decay (energy E_X and absolute emission intensity I_X of the X-rays emitted; maximum kinetic energy E_β of the beta particle emitted) (Firestone and Shirley, 1996; Knoll, 1989; Reus and Westmeier, 1983).

Ni isotope	$T_{1/2}$ [years]	Main production reactions	E_{th} [MeV]	f [%]	Decay mode	Main radiations emitted		
						E_X [keV]	I_X [%]	E_β [keV]
^{59}Ni	$(7.6\pm0.5)\times10^4$	^{58}Ni$(n,\gamma)^{59}$Ni	–	68.077 ± 0.009	EC	6.9	30.4	–
		^{60}Ni$(n,2n)^{59}$Ni	11.6	26.223 ± 0.008		7.7	4.1	
		^{60}Ni$(\gamma,n)^{59}$Ni	11.4					
^{63}Ni	100.1 ± 2.0	^{62}Ni$(n,\gamma)^{63}$Ni	–	3.634 ± 0.002	β^-	–	–	67
		^{64}Ni$(n,2n)^{63}$Ni	9.8	0.926 ± 0.001				
		^{64}Ni$(\gamma,n)^{63}$Ni	9.7					

^{63}Ni isotopes is required before determining their activity concentrations.

The present work describes a radiochemical method adapted for determination of activity concentrations of ^{59}Ni and ^{63}Ni in spent ion-exchange resin and activated charcoal that were withdrawn from the water cleanup system of the IEA-R1 nuclear research reactor, as part of a radioactive waste characterization program currently in progress at IPEN/CNEN-SP.

A method widely employed for purification of Ni is the precipitation with dimethylglyoxime (DMG). In this method, Ni is precipitated in an ammonia solution as a purple chelate complex $Ni(C_4H_7O_2N_2)_2$. Since few metals form complexes with DMG, Ni is selectively separated from other chemical elements using this process (Lehto and Hou, 2011).

Liquid scintillation counting is commonly used in order to determine the activity concentration of ^{63}Ni as a consequence of the high counting efficiency for this radionuclide. However, since it is difficult to identify radionuclides based on continuous beta spectra, it is necessary to separate ^{63}Ni completely from the waste matrix and from other beta-emitters before the measurements (Rosskopfová et al., 2011).

The other long-lived Ni radioactive isotope is ^{59}Ni. It decays by electron capture and can be determined in the same precipitate by X-ray spectrometry using the full-energy peak of 6.9 keV (Fisera and Sebesta, 2010; Gresits and Tölgyesi, 2003).

Based on the results, the separation and purification processes were optimized and the reliability of the measurements was evaluated by the chemical yield of the stable Ni carrier added to the samples in the beginning of the analysis.

Finally, the average value for the ratio of the measured activity concentrations of ^{63}Ni and ^{59}Ni was calculated for both radioactive waste matrices and compared with the theoretical result obtained for the irradiation conditions in the IEA-R1 nuclear research reactor. This comparison is an alternative indicator of the radiochemical method reliability, since the existing data on activity concentrations of ^{59}Ni and ^{63}Ni in spent ion-exchange resins refer to nuclear power reactors (mainly PWR and BWR) (IAEA, 2009) and certified reference materials for these radionuclides are not available.

2. Experimental

2.1. Materials and equipment

Only analytical grade reagents were used during the analyses performed in the scope of the radiochemical method.

Dowex® anionic ion-exchange resin (1 × 4, 50-100 mesh Tyler) and Eichrom Ni resin were purchased from Sigma-Aldrich Inc. and Eichrom Technologies Inc. respectively.

The ^{59}Ni activity concentration was measured using a Low Energy Germanium (LEGe) Detector (model GL2020R) from Canberra Industries. Genie™ 2000 software was used in order to acquire X-ray spectra, as well as to identify and analyze full-energy peaks. ISOCS (In Situ Object Calibration) and LabSOCS (Laboratory Sourceless Object Calibration) software were used in order to perform the efficiency calibration and to discount self-attenuation effects. All mentioned software products are from Camberra Industries. The resolution (FWHM) obtained for the full-energy peak of 6.9 keV was 0.306 keV.

Chemical yield was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Liberty RL Sequential Spectrometer, from Varian Inc.

The ^{63}Ni activity concentration was measured with an automatic HIDEX liquid scintillation counter (model 300SL), using TDCR (triple to double coincidence ratio) and the Ultima-Gold AB™ scintillation cocktail from Perkin Elmer. A ^{63}Ni standard solution (number 105 L 10), provided by Amersham Bioscience and calibrated by the National Laboratory of Metrology of the Ionizing Radiations (LNMRI, Brazil), was used as reference material. MikroWin Hidex 2000 software (from HIDEX, Finland) was used for data acquisition and processing.

2.2. Dissolution of samples

Approximately 2 g of each sample of spent ion-exchange resin previously dried at 80 °C were transferred to Teflon beakers and dissolved with successive additions of concentrated nitric acid, 30% hydrogen peroxide and concentrated perchloric acid, at temperature in the range 250–300 °C. Samples were dried after each addition according to the following sequence: (a) twice with 10 mL of HNO_3 + 5 mL of H_2O_2; (b) once with 10 mL of HNO_3 + 5 mL of $HClO_4$; (c) once with 10 mL of HNO_3 + 5 mL of H_2O_2. After the last addition and drying procedure, the remaining salts were dissolved with 8 mol L^{-1} of HNO_3 and the sample completed with 8 mol L^{-1} HNO_3 in a volumetric flask of 100 mL, forming a stock solution from which the aliquots were taken for the analyses.

Approximately 2 g of activated charcoal were taken from each sample, transferred to porcelain crucibles and calcined progressively in a muffle furnace at a rate of 0.8 °C min^{-1} until reaching 450 °C. This temperature was maintained for 24 h to eliminate from the charcoal sample as much organic matter as possible in order to facilitate the dissolution process. The dissolution process was similar to that used for samples of spent ion-exchange resin, except that $HClO_4$ has been replaced by the same quantity of concentrated HF because of the higher silica content of the samples. Also in this case, after the last addition and drying procedure, the remaining salts were dissolved and the sample completed with 8 mol L^{-1} of HNO_3 in a volumetric flask of 100 mL, forming another stock solution from which the aliquots were taken for the analyses.

2.3. Separation of Ni from interfering radionuclides

2.3.1. Anionic ion-exchange chromatography

An aliquot of the stock solution was transferred to a centrifuge tube, where 2 mL of stable Ni carrier was added from a 1000 mg L^{-1} standard solution traceable to the National Institute of Standard and Technology (NIST, USA). The pH was elevated to 9 using concentrated NH_4OH while precipitation of $Fe(OH)_3$ occurred and Ni remained as a supernatant in the form of an ammonium complex (Rosskopfová et al., 2011).

The precipitate was separated by centrifugation, washed three times with 5 mL of 1:1 NH_4OH solution and reserved for determination of ^{55}Fe.

The supernatant was evaporated to near dryness and the remaining salts were dissolved in 10 mL of 9 mol L^{-1} HCl. This solution was loaded into an anionic ion-exchange resin column 0.8 cm diameter by 10 cm long, previously conditioned with 20 mL of 9 mol L^{-1} HCl (Hou et al., 2005).

Under these conditions, Ni is not adsorbed and passed through the column while the interfering radionuclides (mainly radioactive isotopes of Fe and Co) are retained. The column was washed with 20 mL of 9 mol L^{-1} HCl in increments of 10 mL and the effluent containing Ni was collected in a 150 mL beaker, evaporated to near dryness and the remaining salts were dissolved in 2 mL of 1 mol L^{-1} HCl.

2.3.2. Extraction with chromatographic resin

Eichrom Ni resin (100–150 μm) was left to swell in water and the resulting slurry was loaded into a column 0.8 cm diameter by 10 cm long, previously conditioned with 20 mL of 0.2 mol L^{-1} ammonium citrate (pH=8).

A volume of 2 mL of 1.0 mol L^{-1} ammonium citrate was added to the effluent of the anionic ion-exchange column from the previous step in order to form metal complexes other than Ni, prevent the precipitation of hydroxides after the pH had been increased and to avoid the sorption of those metals to the precipitate of DMG. Concentrated NH_4OH was added slowly until the pH reached between 8 and 9 and the sample was loaded into the prepared Ni resin column. The column was washed with 20 mL of 0.2 mol L^{-1} ammonium citrate (pH=8) to eliminate the interfering radionuclides and the effluent was discarded. Afterward, Ni was eluted from the column with 10 mL of 3 mol L^{-1} HNO_3, diluted to 50 mL with deionized water and the pH was adjusted to 9 with 25% NH_4OH.

Next, 5 mL of 1% DMG solution in ethanol was added to the sample under stirring and then allowed to stand undisturbed until the precipitate settled. The Ni-DMG precipitate was carefully filtered in vacuum using a cellulose acetate filter 47 mm diameter and 0.45 μm porosity, from Sartorius Stedim Biotech GmbH, Germany. A thin and homogeneous surface was thus obtained. The precipitate was washed three times with 3 mL ethanol, dried in a stove at 30 °C for 12 h, placed in a counting support and the activity concentration of ^{59}Ni was measured by X-ray spectrometry using the full-energy peak of 6.9 keV. The efficiency calibration was performed using ISOCS and LabSOCS software. As a standard calibration source of ^{59}Ni is currently unavailable, the measurement results were confirmed using ^{55}Fe precipitated from a standard solution in the same geometry of the samples, because there is no appreciable difference between the detection efficiencies for the X-rays of 5.9 keV (^{55}Fe) and 6.9 keV (^{59}Ni) (Gresits and Tölgyesi, 2003). An average efficiency of 11.5% was obtained for the photon energy of 5.9 keV and since the counting time was between 7200 and 18,000 s, the calculated detection limit (Currie, 1968; Hou et al., 2005) for a sample mass of 1 g and the longest counting time is 0.57 Bq g^{-1}.

After the activity concentration of ^{59}Ni was measured, the filter was removed from the counting support and placed in a glass beaker with 10 mL of 3 mol L^{-1} HNO_3. The precipitate was dissolved and the filter was removed from the beaker using a pair of pincers. The solution was evaporated near dryness at a temperature below 80 °C to avoid the loss of the volatile $Ni(NO_3)_2$, whose boiling point is 137 °C (Hou et al., 2005). The remaining salts were dissolved with 2 mL of deionized water and an aliquot of 0.1 mL was analyzed by ICP-OES to determine the chemical yield of Ni. Finally, the rest of the solution was mixed with 15 mL of the Ultima-Gold AB^{TM} scintillation cocktail and the activity concentration of ^{63}Ni was measured by liquid scintillation counting. The average efficiency for measurements by liquid scintillation counting, in the channel range between 20 and 400 with a duration of 1800 s, was 70% and the calculated detection limit (Currie, 1968; Hou et al., 2005) for a sample mass of 1 g is 5.5 Bq g^{-1}.

2.4. Method validation

The validity of an analytical method is demonstrated by accuracy and precision of the results in comparison with a certified reference material. Due to the unavailability of a reference material containing Ni radioactive isotopes and the lack of a calibration standard of ^{59}Ni, the method validation was based on analyses of three simulated samples, produced by spiking known activities from standard solutions to fresh samples of ion-exchange resins and activated charcoal.

Two simulated samples were produced by spiking known activities of ^{63}Ni and one sample was produced by spiking ^{63}Ni, ^{60}Co and ^{137}Cs with activities of the same magnitude of those found in the actual radioactive waste samples analyzed in the present work.

Background spectra were previously obtained and the number of counts in the channel range 20–400 was compared with the results of a standard solution measured in the same range.

The results of ^{63}Ni activity concentrations for the simulated samples are shown in Table 2. Spiked and measured activity values are in good agreement within experimental uncertainty limits.

Beta spectra of ^{63}Ni obtained from measurements of 1800 s by liquid scintillation counting on the simulated sample S3 are presented in Fig. 1 before and after the use of the anionic ion-exchange resin column. The contrast between these spectra shows the effectiveness of the ion-exchange resin in removing the interfering radionuclides.

3. Results and discussion

The activity concentrations of ^{63}Ni and ^{59}Ni in spent ion-exchange resin and activated charcoal samples, the ratio of these activities and the chemical yield of the stable Ni carrier added in the determination process, are presented in Table 3. Results were corrected to the date of discharge from the water cleanup system of the IEA-R1 nuclear research reactor, considering two different batches: one from 1993 and another from 2003.

Table 2
Activity concentrations of ^{63}Ni in simulated samples produced for method validation and chemical yield of the stable Ni carrier added in the determination process.

Simulated sample	^{63}Ni		Yield [%]
	Spiked [Bq g^{-1}]	Measured [Bq g^{-1}]	
S1 (resin)	520 ± 6	506 ± 19	69
S2 (charcoal)	1034 ± 5	1016 ± 16	90
S3 (charcoal)	1034 ± 5	1050 ± 14	70

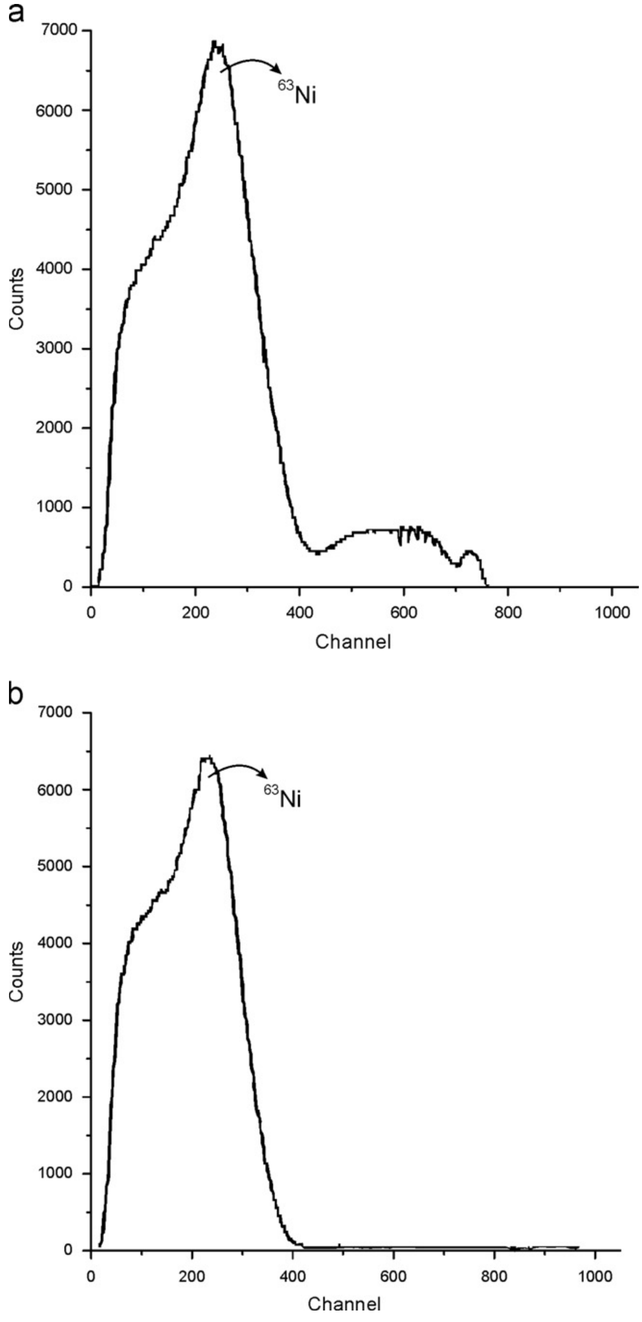

Fig. 1. Beta spectra of ^{63}Ni obtained from measurements of 1800 s by liquid scintillation counting on the simulated sample S3 (a) before and (b) after the use of the anionic ion-exchange resin column.

Once all measurements have been completed, the average value and the corresponding standard deviation were calculated for the ratio of activity concentrations of ^{63}Ni and ^{59}Ni for both matrices of radioactive waste analyzed. The result obtained for spent ion-exchange resin samples was 132 ± 58 and for spent activated charcoal samples the result was 131 ± 66. Considering the experimental standard deviations, these values are in good agreement with the theoretical result 131 ± 11 obtained for the irradiation conditions in the IEA-R1 nuclear research reactor (see Appendix A).

Nevertheless, abnormally low or high values of the ratio of activity concentrations of ^{63}Ni and ^{59}Ni are observed in the data sets of spent ion-exchange resin (samples 1, 5, 12 and 21) and spent activated charcoal (samples 1, 2, 4, 11 and 20). Excluding these nine values, a statistical treatment carried out in order to obtain the uncertainty-weighted mean (Helene and Vanin, 1981) for the ratio of activity concentrations of ^{63}Ni and ^{59}Ni resulted 117 ± 5 for samples of spent ion-exchange resin and 121 ± 6 for samples of spent activated charcoal, which still agree within experimental uncertainty limits when compared to each other and to the theoretical result.

The nine measured values that were previously cited differ considerably from the theoretical value as a consequence of analytical failures due to the following factors: interference of other radionuclides that were not extracted completely during the separation process, high relative uncertainty of the ^{59}Ni activity concentrations that are slightly above the detection limit and eventual inhomogeneity of the Ni-DMG precipitate.

Although the anionic ion-exchange resin column with DMG as a functional group is relatively selective toward Ni, small quantities of ^{60}Co are retained along with Ni. Approximately 5% of the ^{60}Co present in the DMG column load solution is retained and eluted with Ni. As ^{60}Co is present at relatively high activity concentration compared to ^{63}Ni and ^{59}Ni, the presence of even a small portion of the total ^{60}Co in the Ni fraction can result in significant interference (Warwick and Croudace, 2006).

The anionic ion-exchange resin column retains metals that form anionic complexes with Cl^-. However, if the concentrations of the interfering elements are too high, a longer column or even two columns are needed to achieve a complete separation.

Weak acid solutions are employed to extract Ni with DMG, but trivalent and tetravalent metals precipitate at this acidity. As a consequence, Ni extraction is usually performed in basic medium of ammonia with citrate or tartrate to avoid extraction of Cu^{+2} and Co^{+2} and keep heavy metals in solution. Since Fe is present in the waste samples, the use of ammonium citrate hinders the precipitation of $Fe(OH)_3$ and, unlike tartrate, has the advantage of producing no emulsion in a basic medium (Lehto and Hou, 2011). The final precipitate may even contain ^{137}Cs and ^{108m}Ag, which are also present in the analyzed waste samples and that can be removed by carefully washing the precipitate in the chromatographic column.

During the measurements of the activity concentration of ^{63}Ni by liquid scintillation counting, an overlap occurs between its beta spectrum and the Auger electrons spectrum from ^{59}Ni. As long as the ratio of activity concentrations of ^{63}Ni and ^{59}Ni in materials 30 years after irradiation is approximately equal to 100 (Hou et al., 2005), such interference is very small and can be corrected excluding the lower energy channels of the beta spectrum of ^{63}Ni. The most intense Auger electrons emitted by ^{59}Ni have energies in the range from 5.8 keV up to 7.7 keV (Galán, 2010), which are considerably below the maximum kinetic energy of the beta particle emitted by ^{63}Ni (67 keV) (Firestone and Shirley, 1996; Knoll, 1989).

A beta spectrum was obtained for each sample from measurement of 1800 s by liquid scintillation counting using a linear multichannel analyzer. An X-ray spectrum was obtained for each sample from measurements of 7200 up to 18,000 s of live time by X-ray spectrometry. A beta spectrum of ^{63}Ni obtained by liquid scintillation counting is shown in Fig. 2, whereas an X-ray spectrum of ^{59}Ni obtained by X-ray spectrometry is shown in Fig. 3.

4. Conclusion

A radiochemical method to determine the activity concentrations of ^{63}Ni and ^{59}Ni was adapted and applied in the characterization of two radioactive waste matrices from the IEA-R1 nuclear research reactor.

Columns containing anionic ion-exchange resin and chromatographic resin with dimethylglyoxime (DMG) as a functional group were used in order to separate and purify Ni from samples

Table 3
Activity concentrations of ^{63}Ni and ^{59}Ni in spent ion-exchange resin and spent activated charcoal samples, ratio of both specific activities and chemical yield of the stable Ni carrier added in the determination process.

	Spent ion-exchange resin				Spent activated charcoal			
Sample	^{63}Ni [Bq g^{-1}]	^{59}Ni [Bq g^{-1}]	^{63}Ni/^{59}Ni	Yield [%]	^{63}Ni [Bq g^{-1}]	^{59}Ni [Bq g^{-1}]	^{63}Ni/^{59}Ni	Yield [%]
1	16.1 ± 0.5	0.65 ± 0.13	24.8 ± 5.0	85	2260 ± 38	38.8 ± 7.8	58 ± 12	90
2	202 ± 21	1.16 ± 0.25	174 ± 42	72	1520 ± 21	24.3 ± 4.9	63 ± 13	49
3	229 ± 23	1.26 ± 0.25	182 ± 40	71	1180 ± 14	11.0 ± 2.4	107 ± 23	81
4	242 ± 29	1.23 ± 0.26	197 ± 48	83	931.0 ± 6.7	15.6 ± 3.3	60 ± 13	52
5	8875 ± 27	30.0 ± 6.5	296 ± 64	66	1070 ± 14	7.1 ± 1.5	151 ± 32	80
6	3401 ± 12	33.8 ± 7.1	101 ± 21	75	1450 ± 14	9.7 ± 1.9	150 ± 29	97
7	2853 ± 11	26.0 ± 6.1	110 ± 26	77	2340 ± 18	14.6 ± 2.9	160 ± 32	97
8	2248 ± 18	26.4 ± 6.1	85 ± 20	65	1100 ± 18	5.7 ± 1.2	193 ± 41	97
9	2970 ± 18	32.8 ± 6.9	91 ± 19	71	885 ± 12	5.7 ± 1.2	155 ± 33	78
10	4569 ± 44	34.8 ± 7.1	131 ± 27	83	1000 ± 12	7.6 ± 1.6	132 ± 28	71
11	4322 ± 20	47.9 ± 9.9	90 ± 19	88	381.0 ± 7.6	1.0 ± 0.2	381 ± 77	97
12	22.6 ± 1.6	0.63 ± 0.13	36 ± 8	79	3000 ± 21	21.9 ± 5.4	137 ± 28	79
13	242 ± 6	1.67 ± 0.39	145 ± 34	88	1290 ± 15	9.4 ± 1.9	137 ± 28	71
14	263 ± 6	2.98 ± 0.64	88 ± 19	48	2650 ± 19	31.1 ± 6.3	85 ± 17	77
15	2780 ± 21	13.9 ± 3.0	200 ± 43	91	4010 ± 24	26.6 ± 5.4	151 ± 31	68
16	5320 ± 32	39.2 ± 7.9	136 ± 27	91	1160 ± 10	10.3 ± 2.1	113 ± 23	59
17	158 ± 5	1.50 ± 0.30	105 ± 21	79	2740 ± 18	21.6 ± 4.3	127 ± 25	64
18	157 ± 5	1.28 ± 0.26	123 ± 25	80	440.0 ± 6.8	3.0 ± 0.6	147 ± 29	81
19	4250 ± 24	28.8 ± 6.0	148 ± 31	83	399 ± 6	2.8 ± 0.6	143 ± 31	74
20	2800 ± 21	14.4 ± 3.0	194 ± 41	40	859 ± 11	19.4 ± 3.9	44.3 ± 8.9	75
21	4160 ± 34	70.1 ± 14.3	59 ± 12	62	1540 ± 15	9.9 ± 2.0	156 ± 32	77
22	4870 ± 35	42.2 ± 8.6	115 ± 24	94	1150 ± 15	13.5 ± 2.7	85 ± 17	42
23	4890 ± 53	42.3 ± 8.7	116 ± 24	83	1990 ± 18	15.6 ± 3.2	128 ± 26	83
24	2690 ± 21	18.6 ± 3.9	145 ± 30	78	3600 ± 24	39.1 ± 7.8	92 ± 18	69
25	1650 ± 16	11.8 ± 2.5	140 ± 30	63	–	–	–	–
26	206 ± 6	2.06 ± 0.41	100 ± 20	92	–	–	–	–
27	5810 ± 27	26.6 ± 5.5	218 ± 45	83	–	–	–	–
28	287 ± 6	1.89 ± 0.46	152 ± 37	79	–	–	–	–
		Average	**132**			*Average*	**131**	
		SD	**58**			*SD*	**66**	

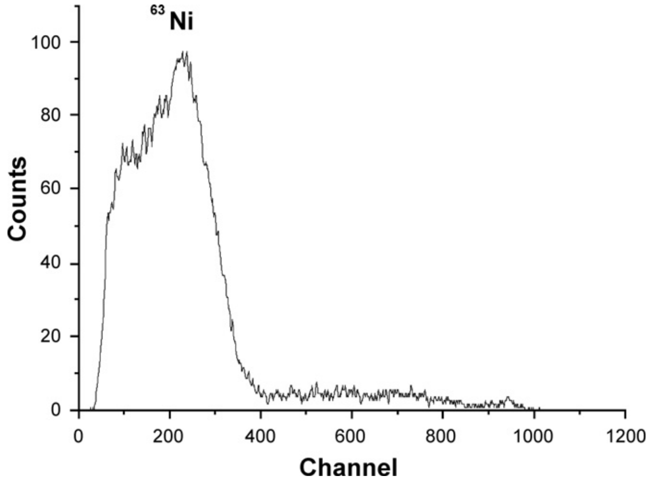

Fig. 2. Beta spectrum of ^{63}Ni obtained from measurement of 1800 s by liquid scintillation counting.

of radioactive wastes consisting of spent ion-exchange resin and activated charcoal. The determination took approximately 3 days to attain the total dissolution of the samples, plus 1 day to complete the analyses with the separation and measurement processes.

Determination of ^{59}Ni by means of X-ray spectrometry employed thin and homogeneous planar sources obtained by precipitation of Ni-DMG and filtration under moderate vacuum using cellulose acetate filters. The reproducibility of the method was assured by the determination of replicates.

High chemical yield of the stable Ni carrier measured by ICP-OES indicates a good overall efficiency of the method.

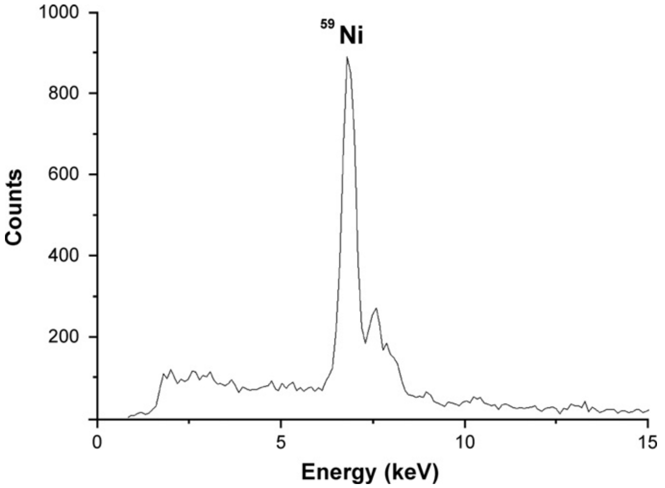

Fig. 3. X-ray spectrum of ^{59}Ni obtained from measurement of 7200 s of live time by X-ray spectrometry.

The average values of the ratio of activity concentrations of ^{63}Ni and ^{59}Ni obtained for spent ion-exchange resin and activated charcoal samples agree well within experimental standard deviations when compared to each other and also when compared to the theoretical result that takes into account the irradiation conditions in the IEA-R1 nuclear research reactor.

These results suggest that the radiochemical method described in the present work is adequate for the determination of ^{63}Ni and ^{59}Ni in both analyzed radioactive waste matrices (spent ion-exchange resin and spent activated charcoal) and can be adopted by a radioactive waste characterization laboratory.

Acknowledgment

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Appendix A. Ratio of ^{63}Ni and ^{59}Ni activities for irradiation in the IEA-R1 nuclear research reactor

In its most general form, the ordinary differential equation that describes the production of a radionuclide by means of irradiation is

$$\frac{d\mathrm{N}}{dt} = N\,\sigma\,\phi\,Vol_i\,e^{-\sigma\phi t} - \lambda\,\mathrm{N} - \sigma'\phi\,\mathrm{N} \tag{1}$$

where N is the number of radionuclide atoms in the sample, N is the number of atoms containing the target nucleus per unit of volume of the sample, σ is the average value of the cross section for the activation nuclear reaction, ϕ is the average value of the particle flux that impinges on the sample, Vol_i is the volume of the sample exposed to the particle flux, λ is the radioactive decay constant of the radionuclide produced by irradiation, σ' is the average value of the total cross section for the absorption of impinging particles by the radionuclide produced by irradiation and t is the total time of irradiation.

If there is no radionuclide at all in the sample before irradiation, Eq. (1) has the solution

$$\mathrm{N} = \frac{N\,\sigma\,\phi\,Vol_i}{\lambda + \phi(\sigma' - \sigma)}\left[e^{-\sigma\phi t} - e^{-(\lambda+\sigma'\phi)t}\right] \tag{2}$$

Considering the irradiation conditions in the IEA-R1 nuclear research reactor and the long half-lives of ^{63}Ni and ^{59}Ni, the products $\sigma\phi t$ and $(\lambda+\sigma'\phi)t$ are both very small, enabling the expansion in series of the exponentials in Eq. (2), from which only the first and the second terms must be taken into account. As a result, Eq. (2) becomes

$$\mathrm{N} = N\,\sigma\,\phi\,Vol_i\,t \tag{3}$$

and the activity of the radionuclide produced is

$$A = N\,\lambda\,\sigma\,\phi\,Vol_i\,t \tag{4}$$

The number of atoms containing the target nucleus per unit of volume of the sample, designed by N, can be written as

$$N = fN_e \tag{5}$$

where f is the isotopic abundance of the target nucleus in the chemical element existent in the sample and N_e is the number of atoms of this chemical element per unit of volume of the sample, both before irradiation.

Therefore, the activity of ^{63}Ni is

$$A_{63} = f_{62}\,N_e\,\lambda_{63}\,\sigma_{62}\,\phi\,Vol_i\,t \tag{6}$$

while the activity of ^{59}Ni is

$$A_{59} = f_{58}\,N_e\,\lambda_{59}\,\sigma_{58}\,\phi\,Vol_i\,t \tag{7}$$

and the ratio of these activities gives

$$\frac{A_{63}}{A_{59}} = \frac{f_{62}\,\lambda_{63}\,\sigma_{62}}{f_{58}\,\lambda_{59}\,\sigma_{58}} \tag{8}$$

where f_{62} is the isotopic abundance of ^{62}Ni and f_{58} is that of ^{58}Ni in natural Ni, λ_{63} is the radioactive decay constant of ^{63}Ni and λ_{59} is that of ^{59}Ni, σ_{62} is the average value of the cross section for the radiative capture reaction ^{62}Ni(n,γ)^{63}Ni and σ_{58} is the average value of the cross section for the radiative capture reaction ^{58}Ni(n,γ)^{59}Ni, because these are the main nuclear reactions that lead to the production of ^{63}Ni and ^{59}Ni. These isotopic abundances and radioactive decay constants can be obtained directly from data presented in Table 1. Radiative capture reactions are caused mostly by thermal neutrons and the values of the cross sections are therefore $\sigma_{62} = 14.5 \pm 0.3$ b and $\sigma_{58} = 4.5 \pm 0.3$ b (Mughabghab, 2003). As a consequence, the ratio of activities calculated by Eq. (8) gives the result

$$\frac{A_{63}}{A_{59}} = 131 \pm 11$$

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