SEPARATION AND QUANTIFICATION OF ^{63}NI FROM ION-EXCHANGE RESIN RADIOACTIVE WASTE

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Abstract

Two methods for ^{63}Ni separation from spent ion-exchange resin samples were carried out, offering a useful methodology to achieve interferences free ^{63}Ni fractions. The two methods consist in resin sample decomposition, pre-treatment and selective separation of ^{63}Ni by using: (1) a single Eichrom®NiResin analytical resin column, named single separation, and (2) two consecutive Eichrom®NiResin analytical resin columns, named double separation. Mineralization by microwave acid digestion and the two ^{63}Ni separation methods thoroughly presented are available. Data processing methods (liquid scintillation cocktail performance evaluation, ^{63}Ni activity assessment, α-β discrimination) to obtain the activity values of α, β-γ, ^{63}Ni emitters and the evaluation of chemical recovery yield of nickel were presented.

Keywords: *^{63}Ni separation, Spent ion-exchange resin, Microwave acid digestion, Extraction chromatography*

Introduction

The ^{63}Ni radioactive isotope is not a naturally occurring radionuclide. The behavior of ^{63}Ni in various media (soil, water, plants, human body and animals) transforms it in a potential hazard to the environment and people if it is not properly disposed. The ability of soil to adsorb ^{63}Ni out of groundwater depends on the soil type and water pH. In general, maximum 1 % of the nickel remains dissolved in the water while the most part is expected to be absorbed by the soil. Plants and animals can take up ^{63}Ni from the soil and propagate it into the food chain. Most of ^{63}Ni radionuclide ingested in the body is excreted within 24 hours, but the part that is absorbed remains for a long time because it tends to be uniformly distributed throughout the body. It is important to characterize the waste containing ^{63}Ni because this radionuclide belongs to those nuclides that dominate the release hazard via groundwater during various times in the future [1].

The ^{63}Ni radioisotope is mainly produced in the structural steels of nuclear reactor vessel and internal components from neutron activation of ^{62}Ni stable isotope. A small fraction released through corrosion of structural components is carried along with cooling water to water clean-up system of reactor: cartridge filters, activated charcoal beds, ion-exchange resin beds [1].

The ^{63}Ni radioisotope is a pure β emitter (E_{max} = 67 keV) with a half-life of 100 years [1]. ^{63}Ni can be detected by liquid scintillation counting (LSC) technique using the quench standard curve method [2], and efficiency tracing with ^{14}C [2, 3]. LSC technique requires separation and purification of ^{63}Ni from the original sample matrices because of its weak beta radiation and interference from coexisting radionuclides.

The spent resin waste streams are produced during routine operations and maintenance at the PHWR CANDU-6, the Canadian type reactors operating at the Romanian Cernavoda Nuclear Power Plant (NPP) [4].

The ion-exchange resins used in purification systems at Cernavoda NPP consist of a cross-linked resin matrix produced by co-polymerizing styrene with divinylbenzene, containing sulfonic acid functional group (for strong acid cation resin, Amberlite™ iRN-77) and quaternary ammonium functional group (for strong base anion resin, Amberlite™ IRN-78). Also, Amberlite™ IRN-150 (a nominal 1:1 chemical equivalent mixture of IRN-77 and IRN-78), and Amberlite™ IRN-154 (a similar mixture of acid and base resins, but with Li^+ substituting for approximately 75 % of H^+ on the strong acid cation-exchange resin) are used [5].

The spent resin waste, transferred from Cernavoda NPP and used in this study for separation and quantification of ^{63}Ni, was sampled from a spent ion-exchange resin drum coming from the sieves of both moderator and primary heat transport purification system.

The microwave digestion process was employed in order to transfer the ^{63}Ni radionuclide into solution and thus the separation methods could be applied.

The experimental studies were carried out by using Eichrom®NiResin analytical resin and the potential of two different methodologies for ^{63}Ni separation from Cernavoda NPP spent ion-exchange resin was studied: (1) a single Ni-selective resin column, named single separation, and (2) two consecutive Ni-selective resin columns, named double separation

Methodology

The experiment (depicted in Fig. 1) consists in samples preparation, ^{63}Ni separation and data processing and interpretation.

Mineralization of spent ion-exchange resin matrix by microwave acid digestion

A Berghof^{TM}Speedwave$^{®}$ four microwave acid digestion system was used to decompose the spent resin samples. A total of 1.2 g spent ion-exchange resin was sampled and divided into 6 aliquots of 0.2 g (marked as S1, S2…S6) and placed into the digestion vessels. Two 0.2 g aliquots (S5, S6) were used to measure α-β global activity and the other four aliquots (S1...S4) were used in ^{63}Ni separation processes, i.e. duplicates for each of the two ^{63}Ni separation methods. Two mg/aliquots of Ni^{2+} (0.2 mL of a 10 mg mL^{-1} solution prepared by dissolving $NiCl_2{\cdot}6H_2O$ in distilled water) were added to the (S1...S4) sample as a stable yield tracer, and 10 mL of concentrated reagents (HNO_3:H_2O_2 = 4:1) were used for each of the six aliquots as a digestion mixture.The digestion program was performed in two work steps and it was completed in 130 minutes. The operational parameters of the microwave equipment applied to graphite mineralization are presented in Table 1.

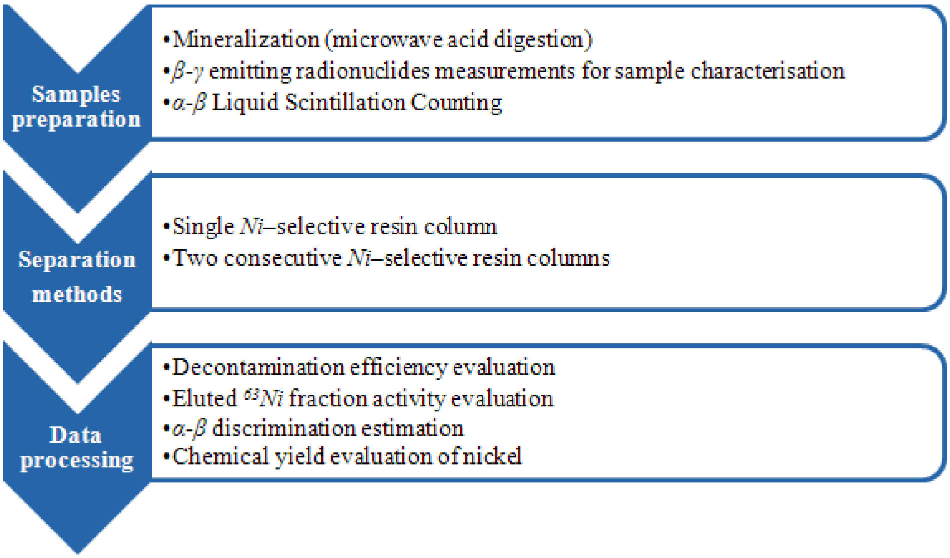

Fig.1. The ^{60}Ni separation and quantification experiment concept

Table 1. Operational parameters of microwave acid digestion procedure

Step no.	Set point temperature T [^{0}C]	Maximum allowed pressure P [bar]	Slope (ramp time of program step) [min]	Time for which T is kept constant [min]	Electrical power [%]
1	200	40	20	10	70
	230	40	10	30	70
	50	40	10	10	0
2	135	40	10	10	70
	200	40	10	20	70
	230	40	10	40	70
	50	40	10	10	0

Mineralized samples preparation for γ and LSC measurements

Each of the S1...S6 mineralized resin sample aliquots was filtered and evaporated to near dryness on a hotplate, and the residue was dissolved with 10 mL of 1.0 M HNO_3 solution, and transferred to a 20 mL low diffusion polyethylene scintillation vial (LSC vial). Three milliliters of solution from S5 and S6 vials were taken and mixed with 15 mL of Ultima Gold™ AB liquid scintillation cocktail for α-β global counting with LSC technique. The other vials were measured by γ spectrometry for the initial evaluation of the interfering radionuclides activity in the spent resin.

Separation of ^{63}Ni from interfering radionuclides

The Eichrom$^{®}$NiResin is mainly used for Ni^{2+} separation on the base an extraction system that presents selectivity for nickel. This extraction chromatographic resin is based on an precipitation of nickel with dimethylglyoxime (DMG) at pH 8-9 resulting a $Ni(DMG)_2$ complex that is insoluble in water [6].

^{63}Ni single separation

The S1 and S2 samples were evaporated to near dryness and converted to chloride form by repeated evaporations with concentrated hydrochloric acid solution.

The HCl solution is preferred to the HNO_3 solution because the nickel chloride ($NiCl_2$) is not volatile compared to nickel nitrate, $Ni(NO_3)_2{\cdot}6H_2O$, that has a boiling point of 137 ^{0}C. The residue was dissolved in 1M hydrochloric acid, a solution of 0.2 M ammonium citrate was added and the overall solution was adjusted to pH 8-9 with concentrated ammonium hydroxide. The presence of the ammonium citrate prevents any co-precipitation of metal ions that would precipitate as insoluble hydroxides, making the separation process impossible. The pH was adjusted to 8-9 with ammonium hydroxide before loading the resin because the complex of Ni with DMG is stable at pH 7-12 [6].

The Eichrom®NiResin was conditioned with a 0.2 M ammonium citrate solution adjusted to pH 8-9 and packed into 5 mL polypropylene columns.

The S1 and S2 samples were loaded on the columns and let flow by gravity. When the samples were loaded on the resin, a red precipitate of $Ni(DMG)_2$ appeared.

Twenty milliliters of 0.2 M ammonium citrate solution at pH 8-9 were used for washing resin columns to remove the matrix interferences. The $Ni(DMG)_2$ complex was dissolved with 20 mL of 3M HNO_3 solution, allowing its elution from the resin. After $Ni(DMG)_2$ elution, the resin colour is changed back to white and the eluted solution is colourless. Most of the initial DMG quantity coated on the inert support has been eluted as the $Ni(DMG)_2$ complex, therefore the resin is not suitable for reuse [6]. The eluted ^{63}Ni fractions were evaporated to 0.2-0.3 mL and transferred to LSC vials with 13 mL of 1M HNO_3 solution for measurements by γ, LSC and ICP-OE spectrometry. The radiochemical procedure is schematically shown in Fig.2.

^{63}Ni double separation

Four Eichrom®NiResin columns were prepared for the S3 and S4 samples, following the same procedure as for the single separation method. Two consecutive separations were performed according to the radiochemical procedure schematically shown in Fig. 2.

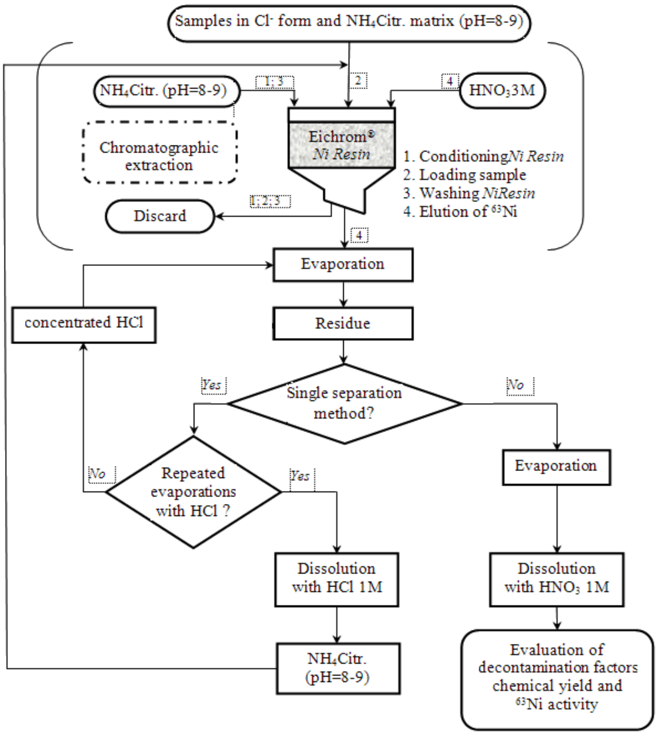

Fig.2. Flow chart for ^{63}Ni single separation and ^{63}Ni double separation

Eluted ^{63}Ni fraction measurements

After the separation methods were performed, 3 mL of each 13 mL solution were taken and mixed with 15 mL of UltimaGold™ AB liquid scintillation cocktail for ^{63}Ni LSC measurements, the remained 10 ml were used for measurements by γ spectrometry, and finally 0.25 ml of solution were sampled after γ measurements and dilutions were prepared to have a final nickel mass concentration spanning [0…4] $mg{\cdot}L^{-1}$ for ICP-OES chemical recovery yield measurements.

^{63}Ni activity measurements were performed using LSC technique in the (0-67) keV energy range, under normal count mode with an acquisition time of 60 min for each sample. DPM activities were calculated as a ratio between the CPM net count rate and the LSC efficiency that was evaluated on the base of quench correction curve obtaining by using 10 standards in different quench levels (Fig.3).

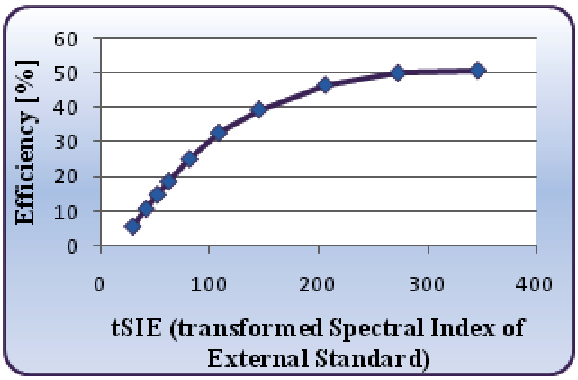

Fig. 3. Quench correction curves of ^{63}Ni

Results and discussion

Decontamination factors evaluation

By γ spectrometry, the analyses were performed on the solutions recovered after both mineralization and at the end of the chemical treatment methods. A high purity germanium detector HPGe (EG&G Ortec, USA) was used for estimating the γ emitting radionuclides activity in samples.

The samples resulted by mineralization process of the resin matrix contain the β -γ emitters ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs in the following activity ratios: ^{54}Mn: ^{60}Co: ^{134}Cs: ^{137}Cs = 1:75:23:1995.

The β-γ emitters activity measurements in the purified solutions resulted by applying the two separation method showed a very high efficiency with regard to ^{54}Mn and ^{134}Cs (for single separation) and ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs(for double separation). The activities of these radionuclides were below the minimum detectable activity (see Table 2), which corresponds to a decontamination efficiency presumed to be almost 100 %.

Table 2. Minimum detectable activity (MDA) values for β-γ nuclides

Method	MDA [Bq mL^{-1}]			
	^{54}Mn	^{60}Co	^{134}Cs	^{137}Cs
Single separation	2.78x10^{-2}	2.92x10^{-2}	2.54x10^{-2}	2.82x10^{-2}
Double separation	2.74x10^{-2}	2.81x10^{-2}	2.44x10^{-2}	2.92x10^{-2}

For β-γ emitters in ^{63}Ni fractions (^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs), the decontamination factors and decontamination efficiencies values are presented in Table 3.

Table 3. Decontamination factors, DF, and decontamination efficiencies, DE [%] for the two separation methods

Method		^{54}Mn	^{60}Co	^{134}Cs	^{137}Cs
Single separation	*DF*	> 3	12.42	> 89	6470
	DE [%]	≈100	91.94	≈100	99.98
Double separation	*DF*	> 3	> 270	> 90	> 6500
	DE [%]	≈100	≈100	≈100	≈100

Evaluation of liquid scintillation cocktail performance

Sample preparation is a critical step in obtaining accurate results in LSC process. The compatibility between the liquid scintillation cocktail and sample to be measured is the primary criterion for choosing scintillation cocktail. A good phase contact has to achieve by obtaining stable, clear and homogeneous solutions of sample -scintillation cocktail for LSC technique. The second criterion that affects quality of the LSC measurement is related to both the counting efficiency and the sample holding capacity of the liquid scintillation cocktail [3].

All the purified sample – liquid scintilation cocktail emulsions, resulted from the two separation methods, were homogeneous and colourless, allowing an efficient transfer of the energy between beta particles and cocktail solution.

Counting efficiency assessment of Ultima Gold® AB scintillation cocktail versus sample load was accomplished by using three samples prepared from ^{63}Ni fraction eluted in the first experiment (^{63}Ni single separation).

The Ultima Gold®AB scintillation cocktail records low loss in efficiency in the presence of 1M HNO$_3$ matrix, from 63 % to 56 % with increasing sample loading capacity from 6.25 % (1 mL sample) to 18.75 % (3 mL sample). Therefore, this type of liquid scintillation cocktail offers a very good counting performance in the (1...3) mL sample volume range (see Fig.4).

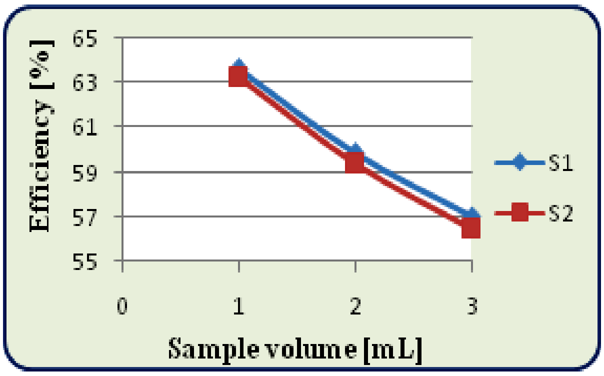

Fig. 4. Counting efficiency versus sample load

Eluted ^{63}Ni fractions activity

The values of ^{63}Ni activity in purified fractions achieved by application of the two separation methods are presented in Table 4.

Table 4. ^{63}Ni activity values in purified fractions

Method	Sample	^{63}Ni [Bq mL^{-1}]	Average [Bq mL^{-1}]
Single separation	S1	19.62	20.23
	S2	20.84	
Double separation	S3	20.26	20.95
	S4	21.63	

Minimum detectable activity

Minimum detectable activity (MDA) is a mathematical function of background counts, counting time of background and samples, counting efficiency and sample volume for analysis [7].

A volume of 3 mL per sample and a counting time of 60 min for both samples and background were used to achieve the MDA values. For the two^{63}Ni separation methods, the MDA values were lower than 0.03 Bq mL^{-1}. These MDA values are 700 times lower than the ^{63}Ni activity in eluted fractions (see Fig.5). It reveals that the LSC technique can be used to assess the ^{63}Ni activity in the ion-exchange resin samples after the radiochemical purification of ^{63}Ni.

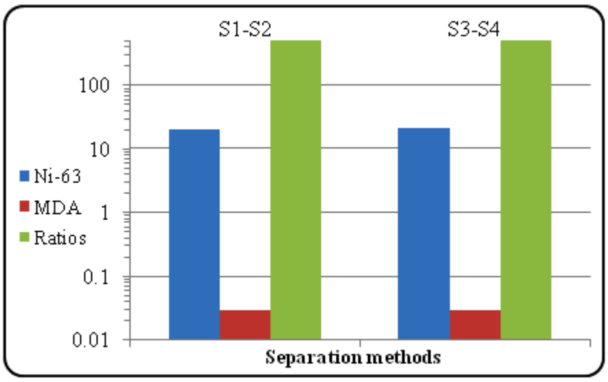

Fig. 5. Logarithmic scale representations of ^{63}Ni activity concentration [Bq mL^{-1}], MDA values [Bq mL^{-1}] and their ratios

Chemical yield evaluation of nickel

A Berghof^{TM}iCAP 6500 series inductively coupled plasma-optical emission (ICP-OE) spectrometer was used for stable Ni^{2+}carrier concentration measurements before and after chemical separation. The values of nickel recovery yield (summarized in Fig.6) are reproducible for each separation method, spanning from 90.20 % to 95.73 %, with an average value of 92.68 %.

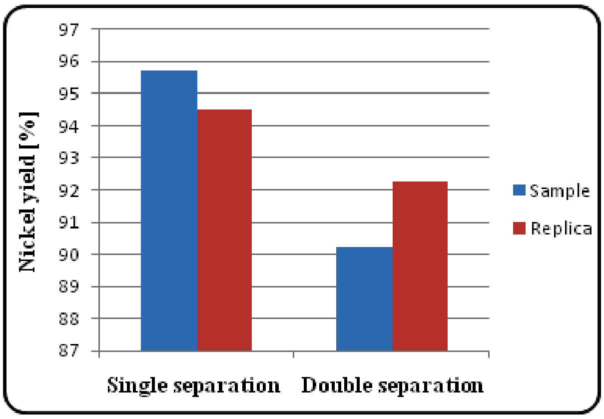

Fig. 6. Nickel recovery yields for (S1…S4) samples

Total α-β activity discrimination evaluation

The alpha spectra in the samples (S5, S6) before separationand the beta spectra after ^{63}Ni separation (S1 and S2) are depicted in Fig.7. In (150...240) keV region, activity of purified samples presents values of background comparative to α activity values in (S5, S6) samples.

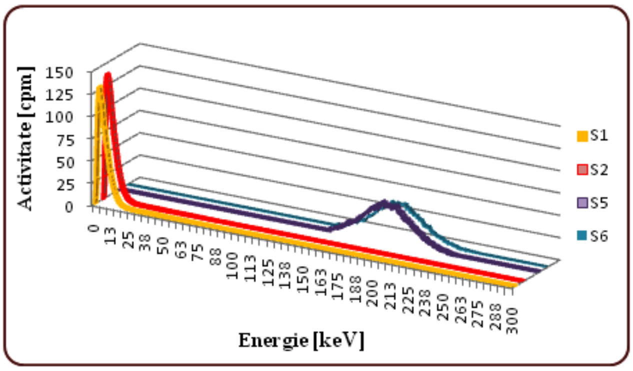

Fig. 7. α, β radionuclides spectra before and after ^{63}Ni separation

The quenching level in sample (which is indicated by tSIE parameter – transformed Spectral Index of the External standard) determines the alpha peaks region. For all purified samples resulted by performing the two ^{63}Ni separation methods, the tSIE values are higher than 260. At these tSIE values, it is expected that a potential presence of α emitters to be found between 150 keV and 500 keV.

Conclusions

For pre-treatment technique, microwave acid digestion proved to be an easy, rapid and reliable method for dissolution of the spent resin samples.

The results achieved by performing the two ^{63}Ni separation and purification methods, with the aim of ^{63}Ni activity quantification in spent ion-exchange resin samples, reveal that double separation represents an interferences free ^{63}Ni separation method, obtaining very good decontamination efficiencies value (practically 100 %). For this method, γ spectrometric measurements of purified fractions did not detect the presence of β-γ emitters. After separation, ^{63}Ni activities higher than 0.03 Bq mL^{-1} value can be estimated by applying LSC technique.

Alpha interfering nuclides can be removed by using the two methods.

The average chemical recovery yield, for each of the performed separation technique, exceeded 90 %; therefore these methods can be easily applied to samples with smaller quantities of ^{63}Ni activity.

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