INFLUENCE OF ^{60}CO IN SEPARATION, PURIFICATION, AND QUANTIFICATION OF ^{63}NI FROM RADIOACTIVE WASTE SAMPLES

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Abstract

This study presents an efficient approach to select the most suitable ^{63}Ni separation methodology according to ^{60}Co activity concentration from liquid radioactive waste generated by TRIGA reactor operation. To accomplish this goal, two methodologies were investigated for ^{63}Ni separation: (1) two consecutive Ni-selective resin columns, double separation, and (2) ion-exchange chromatography, followed by extraction chromatography using Ni resin column. The experimental tests were realized using standard solutions with known activity concentrations of ^{63}Ni and ^{60}Co. Based on the results achieved in this study it is recommended the 2nd method because it is more efficient for the ^{63}Ni separation from interfering radionuclides, especially from ^{60}Co interference. The decontamination efficiency of ^{60}Co for this method is around 98% and the chemical yield for Ni is over 95%.

Keywords: *Gamma spectrometry, Liquid scintillation cocktail spectrometry, Ni-63 separation methods*

Introduction

All the radioactive waste amounts generated from the TRIGA reactor operation are stored as institutional radioactive waste at the National Repository Băița Bihor according to the waste acceptance criteria. ^{63}Ni is one of the difficult-to-measure radionuclides that need to be evaluated for the safe disposal of the institutional radioactive waste generated both from the operation and decommissioning activities of the TRIGA reactor.

^{63}Ni and ^{60}Co radioisotopes are mainly produced in the structural steels of nuclear reactor vessel and internal components from neutron activation of ^{62}Ni and ^{59}Co stable isotopes. A small fraction released through corrosion of structural components is carried along with cooling water to water clean-up system of the reactor: cartridge filters, activated charcoal beds, ion-exchange resin beds [1].

^{63}Ni is a pure beta-emitting radionuclide with no emission of gamma-rays, which needs to be chemically separated from the interference radionuclides contained in the radioactive waste samples previous to liquid scintillation cocktail (LSC) spectrometry measurements [2].

^{60}Co isotope emits two energetic γ rays of 1.17 MeV and 1.33 MeV, but it also undergoes β^- emission decay (E_{max} = 1480 keV) to a stable ^{60}Ni nucleus. More than 95 % of the radioactive decay results in β particle energies lower than 314 keV, with an average of only 94 keV per ^{60}Co disintegration [1].

The accuracy of LSC measurements depends on the efficiency of the radiochemical separation of the interest nuclide from other beta-emitting radionuclides.

Therefore, ^{60}Co presence in the ^{63}Ni fraction measured by the LSC technique can result in significant interference.

The main interference radionuclide in the ^{63}Ni quantification by LSC measurements, ^{60}Co, is retained on Ni resin columns and eluate with ^{63}Ni activity concentration, according to the research studies related to the Ni separation by extraction chromatography using Ni resin columns from the liquid radioactive waste samples carried out thus far in RATEN ICN.

Also, Warwick and al. assert in their studies [3] that 5% of the activity concentration of ^{60}Co present in the elution samples resulted from the purification of ^{63}Ni by extraction chromatography using Ni resin.

As ^{60}Co is the main contributor gamma radionuclide to the total activity concentration of the radioactive waste generated from TRIGA reactor operation, ^{63}Ni separation methods need to be adapted according to ^{60}Co activity concentration to obtain an accurate separation of ^{63}Ni from the interfering radionuclides.

Therefore, the purpose of this study is to select the most suitable radiochemical protocol for ^{63}Ni separation from the interfering radionuclides, according to the ^{60}Co activity concentration in the sample.

Taking into consideration that ^{60}Co is an easy-to-measure radionuclide by gamma spectrometry, the selection of ^{63}Ni separation method with high decontamination factors can be established in an efficient manner and without any preliminary experimental tests based on ^{60}Co activity concentration.

Experimental set-up

To accomplish the goal of this study, two methodologies for ^{63}Ni separation were achieved:

(1) two consecutive Ni-selective resin columns, double separation, and

(2) ion-exchange chromatography, followed by extraction chromatography using Ni resin column.

A stock solution was gravimetrically spiked with a known amount of ^{63}Ni and ^{60}Co standard solution, prepared from individual solutions with activity concentration of radionuclides. Two aliquot samples from the stock solution were used as initial samples in the experimental tests performed.

At the beginning of each experiment 1 mL of Ni^{2+} carrier, in the form of 1000 mg/L multi-element standard solution, was added, to assess the recovery yield of each proposed methodology. The Ni^{2+} concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

Figures 1 and 2 are schematically present the main steps performed for the two methodologies applied in this study. The first methodology (M1) involves a double process of Ni separation and purification using Ni selective resin, while the 2nd methodology (M2) involves a Ni separation using AG 1-X8 strongly basic anion exchange resin followed by Ni purification on Ni resin.

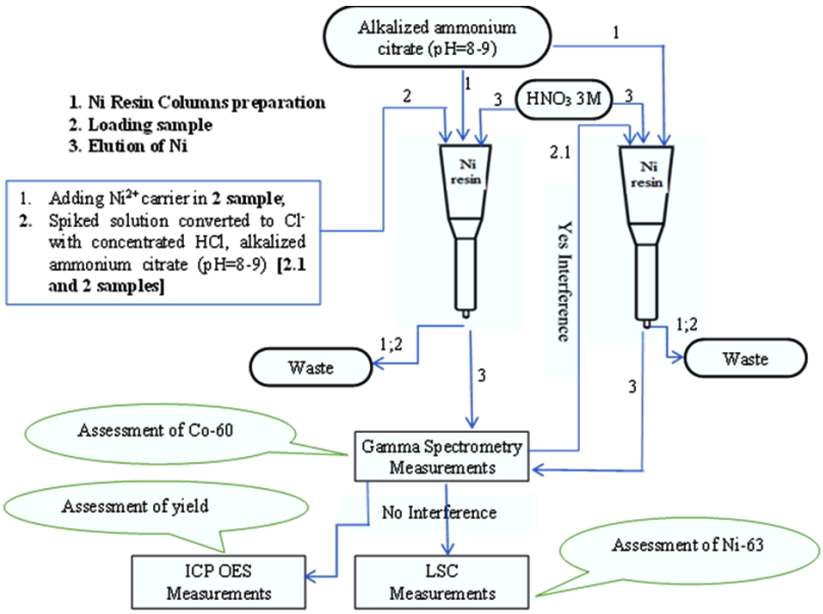


Fig. 1. Flow chart of method M1 for Ni separation and purification process using selective Ni resin

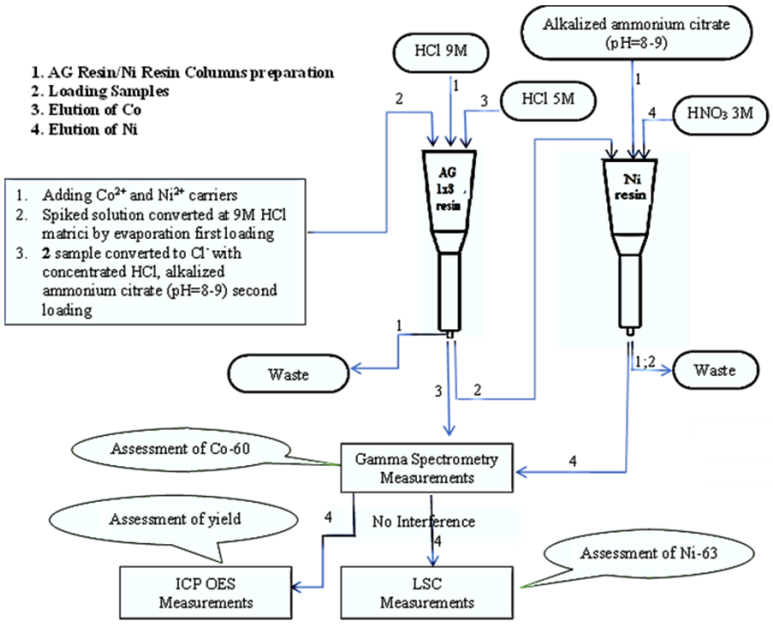


Fig. 2. Flow chart of method M2 for Ni separation using AG 1-X8 resin and Ni purification using Ni resin

The Nickel selective specific resin (100-150 µm particle size, Triskem International, France) consists of a dimethylglyoxime extractant coated on an inert support and it is based on an on-column precipitation of Ni^{2+} ions with dimethylglyoxime (DMG). The Ni-dimethylglyoxime complex, Ni $(DMG)_2$, is insoluble in water, with a high stability constant [4]. During the precipitation reaction two dimethylglyoxime molecules react with Ni^{2+} ions and a red precipitate appears on the resin (Fig. 3) which disappears with Ni elution.

The use of Analytical Grade AG®1-X8 strongly basic anion exchange resin (100-200 mesh particle size, chloride form; total capacity of 1.2 me mL^{-1} resin bed) implies the presence of the anionic complex formed by cobalt ion with chloride ion in high concentration of hydrochloric acid solution [5]. It can be observed in Fig. 3 the columns resulted after uploading the samples on Ni resin (red colour) and AG1-X8 (green colour).

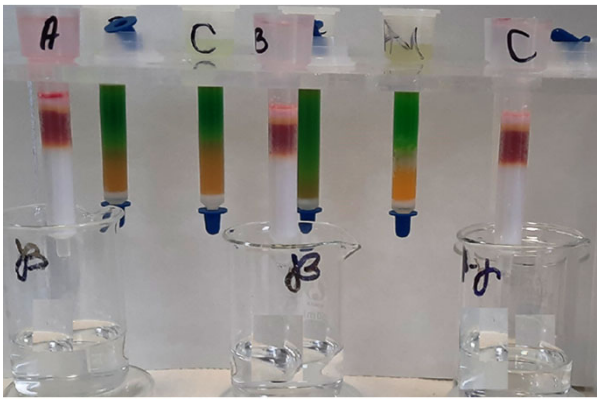


Fig. 3. The Ni resin and AG1x8 resin columns after samples uploading

The Ni resin columns were conditioned with 10 ml diammonium hydrogen citrate adjusted to 8-9 pH and the AG 1-X8 resin column was conditioned with HCl concentration 9M. The elution of Ni was realized using 3M HNO_3 and for Co elution 5M HCl was used. A volume of 3 ml from the Ni elution samples was mixed with Ultima Gold AB scintillation cocktail and was measured by LSC using a TRICARB model. The LSC is the most suitable method for low energy beta emitters' determination which has a high counting efficiency [6].

Aliquot samples, from Ni elution samples, were prepared in 2% HNO_3 ultrapure for ICP OES measurements. The ICP OES measurements were performed in the concentration range of 0.1 ppm -1 ppm. The correlation coefficient obtained between concentration and signal emitted by ICP-OES was 0.999955 meaning a very good correlation.

The gamma spectrometry measurements were performed in TRICARB vial glass geometries at the contact with a coaxial GeHP detector. All the sub-samples resulted from separation and purification steps from both experiments were analysed by gamma spectrometry to establish the activity concentration of ^{60}Co.

Results and discussion

The ^{60}Co activity concentration was followed after each separation process carried out either on Ni resin or AG1-X8 resin columns, and also after the Ni purification process was accomplished for the two methodologies studied. The initial, elution, and effluent samples were analysed by gamma measurements using a GeHP detector (values reported in Table 1). The characteristic energetic spectra of the samples were acquired using GammaVision software and analysed by GENIE2000 software.

The values reported of ^{60}Co activity for all the samples resulted from the separation step of the two methodologies (M1 and M2) performed are presented in Table 1.

Table 1. ^{60}Co activity concentration resulted after the separation step

Methodologies / Samples	**^{60}Co Activity Concentration [Bq]**		
	Initial	Elution	Effluent
M1	3112.28±34.02	329.45±4.24	2713.8±30.63
M2	3239.00±35.40	2512.91±28.15	773.93±9.75

The elution sample resulted from the separation process on the AG 1-X8 resin column (M2), contains only ^{60}Co retained on the AG 1-X8 resin column, while the effluent sample contains ^{63}Ni and the rest of the ^{60}Co radioactivity.

The elution sample resulted after the first separation process on the Ni resin column (M1) contains ^{63}Ni and some ^{60}Co retained and eluted together with ^{63}Ni on Ni resin. From Table 1 it can be observed that the Co also forms a stable complex with the DMG of the resin and thereby interferes in the Ni separation being necessary to apply another purification process of Ni.

^{60}Co activity identified in the elution and effluent samples resulted after the ^{63}Ni purification step using Ni resin is presented in Table 2.

In the purification step, the loading samples on Ni resin were the elution sample for M1 and the effluent sample for M2 resulting from the separation step (highlighted by green and blue colour in Tables 1 and 2).

Table 2. ^{60}Co activity concentration resulted after the purification step

Methodologies / Samples	**^{60}Co Activity Concentration [Bq]**	
	Elution	Effluent
M1	63.24±1.58	214.57±3.57
M2	40.16±1.06	722.53±9.93

About 10% of ^{60}Co activity concentration was found to be retained in Ni resin during the separation step and 19% on the purification step performed in M1. Although the ^{60}Co activity concentration is not completely removed from the ^{63}Ni elution samples, we consider the influence of ^{60}Co radionuclide on the accuracy of the LSC measurements to be negligible due to its presence in small concentrations compared with ^{63}Ni activity concentrations.

In the experimental tests performed the performance parameters of the proposed methods, consisting of decontamination efficiency/factors for ^{60}Co and chemical yields for ^{63}Ni, were assessed. The performance factors for ^{60}Co were assessed for each step performed (separation and purification).

The decontamination efficiency and the decontamination factor are defined in the following by Eqs. (1) and (2):

$$D.E. = 100 - \left[\left(A_f / A_i\right) \cdot 100\right] \quad (1)$$

$$D.F. = A_i / A_f \quad (2)$$

where:
A_f = ^{60}Co final activity concentration obtained in elution or effluent samples depending on the applied methodology [Bq]
A_i = ^{60}Co activity concentration in the initial samples [Bq].

The decontamination efficiency (D.E) and decontamination factor (D.F) values are presented in Table 3. The results show an increase of the decontamination efficiency values between the separation and purification step, for both methodologies applied. After the purification step, around 98% for M1 and 99 % for M2 decontamination efficiency values were obtained, which demonstrates very good efficiency decontamination of ^{60}Co for both methodologies.

It is also observed an increase in the D.F. values obtained after each separation and purification step. The D.F. value obtained in the purification step for M2 (80.66) is higher than the one for M1 (49.21).

However, the economic factor is one of the selection criteria of a characterization methodology, and in our case, the M2 method proposed is more cost-effective when take considering the acquisition price of AG resin in comparison to the price of Ni resin.

Another performance parameter of the Ni separation and purification process is the recovery yield that is calculated by using equation Eq. (3) based on the initial and elution samples concentration activity.

The recovery yield can be calculated based on the activity concentration of the interest radionuclide and also, on the concentration of the stable element introduced at the beginning of the experimental test.

$$\eta = \left(A_f / A_i\right) \cdot 100 \quad \text{or} \quad \eta = \left(m_f / m_i\right) \cdot 100 \quad (3)$$

where:
A_f = ^{63}Ni activity concentration obtained in elution samples [Bq]
A_i = ^{63}Ni activity concentration in the initial samples [Bq]
m_f = Ni^{2+} final concentration obtained in elution samples by ICP OES measurements [Bq]
m_i = Ni^{2+} initial concentration added at the beginning of the experiment tests [Bq].

A volume of 3 ml elution sample was mixed with 15 ml Ultima Gold AB scintillation cocktail in a 20 mL polyethylene vial and, for a count time of 120 seconds, the spectrum sample was acquired in 0-67 keV energetic regions (see Fig. 4).

Table 3. The performance factors of the applied methodologies

^{60}Co Methodologies	**Decontamination Efficiency (%)**		**Decontamination Factor**	
	Separation step	Purification step	Separation step	Purification step
M1	89.41	97.97	9.45	49.21
M2	76.11	98.76	4.19	80.66

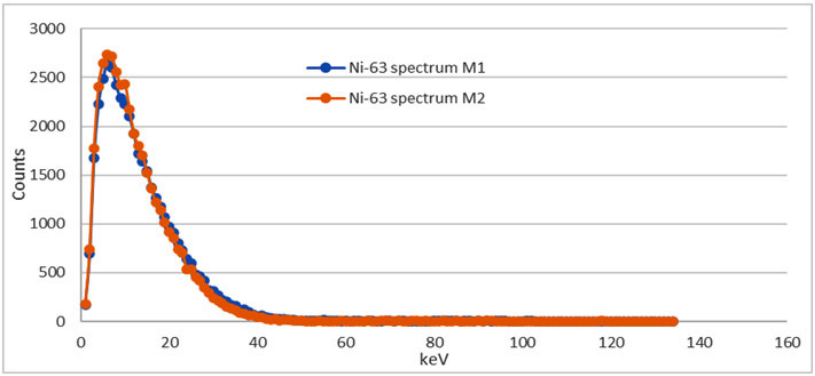


Fig. 4. ^{63}Ni energetic spectra of the elution samples resulted from M1 and M2

The ^{63}Ni activity concentration was calculated based on the counting efficiency and the count per second (cpm) values determined by LSC spectrometry measurements using appropriate quench curves.

The counting efficiencies values determined by LSC for the ^{63}Ni elution samples analysed were 65.97% (M1) and 65.47 % (M2). The ^{63}Ni activity concentration in the elution samples resulted after the purification step on Ni resin and the recovery yield is listed in Table 4.

Table 4. ^{63}Ni activity concentration and the radioactive recovery yield

Methodologies / Samples	^{63}Ni Activity concentration [Bq]		Radioactive recovery yield [%]
	Initial	Elution	
M1	5607.26±18.50	5579.43±27.34	99.35
M2	5835.58±19.26	5728.93±28.07	98.59

Table 5. Ni^{2+} concentration and the chemical recovery yield by ICP OES measurements

Methodologies / Samples	Ni^{2+} Activity concentration [Bq]		Radioactive recovery yield [%]
	Theoretical	Experimental	
M1	1.007	0.999064	99.21
M2	1.019	1.003116	98.44

The obtained data for M1 and M2 regarding the nickel activity concentration are very close and the recovery yield for each methodology is over 95%.

The recovery yield was also calculated using the Ni^{2+} concentration obtained at ICP OES measurements. The theoretical and experimental concentration of Ni^{2+} and the recovery yield obtained for both applied methodologies are presented in Table 5. The radioactive and chemical recovery yield values obtained are almost similar, around 99% for M1 and 98% for M2.

Recent studies have reported that the AG 1-X8 resin is very efficient for nickel separation from transitional metals such as Co^{2+}, Cu^{2+}, $Fe^{3+,}$ and Zn^{2+} that form anion complexes with Cl^- in different concentrations of HCl solutions, while the rare earth elements present in the sample matrix don't form stable anion complexes with Cl^- and there are present in effluent sample together with ^{63}Ni activity concentration. For these radionuclides a further purification of the Ni fraction using a Ni resin column to accurately quantify the activity concentration of ^{63}Ni by LSC [6]. Removing Co, Cu, Zn, and Fe elements in the separation step will avoid the competition of these elements with Ni for the available DMG on the column in the purification step and the ^{63}Ni elution samples will be free of interfering radionuclides or in insignificant concentrations.

Also, the selective Ni resin is used in the separation step of nickel from the other interfering radionuclides such as Co, Cu, Fe, Ca, Pt, and Pb but in our study, we demonstrate that the Co activity is retained in Ni resin by forming a stable complex with dimethylglyoxime extracted material, and also need a further purification of Ni fraction.

Considering the results obtained in this study and the fact that the radioactive waste generated by TRIGA rector are complex matrices that need to be characterized, we consider the M2 methodology as being more efficient for Ni separation from the interfering radionuclides existing in the radioactive waste samples.

Conclusions

The data presented in this article revealed the conditions under which the interferences-free Ni separation could be achieved. Both radiochemical methodologies studied are efficient and can be successfully applied for ^{63}Ni separation and purification process. However, for radioactive samples with a high activity concentration of ^{60}Co, we recommend the M2 methodology because AG1-X8 resin retains around 80% of ^{60}Co activity concentration, thus the degree of retention on Ni resin in purification step decreases.

The results obtained proved that the methodology M2, based on ion exchange chromatography separation using AG1-X8 resin provides better values for the performance parameters, and the retention degree of ^{60}Co on AG resin (87%). It is also more cost-effective taking into account the lower purchase price of the AG 1-X8 resin in comparison to the Ni resin one.

The ^{60}Co decontamination efficiency value obtained for this method is around 94% and the chemical yield for Ni is over 95%.

The results obtained in this study will be used in the optimization of the radiochemical methods applied for ^{63}Ni separation and purification from radioactive waste samples generated from TRIGA reactor operation and decommissioning activities.

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