

DETERMINATION OF ^{55}Fe AND ^{63}Ni IN SPENT ION-EXCHANGE RESINS FROM THE IEA-R1 REACTOR (IPEN-CNEN/SP)

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ABSTRACT

Iron and nickel are used in a wide range of metallic alloys employed in reactor core structures and their corresponding activation products are often encountered in reactor-derived solid low-level wastes and effluents. Both ^{63}Ni and ^{55}Fe are neutron activation products. ^{63}Ni is produced by a neutron-gamma reaction of ^{62}Ni and by a neutron-proton reaction of ^{63}Cu . Iron-55 is produced by neutron activation of two major stable iron isotopes: neutron-gamma reaction of ^{54}Fe and neutron-to-neutron reaction of ^{56}Fe . Nickel-63 is a pure beta emitter with maximum energy of 66.95 keV and half-life of 100.1 years, and ^{55}Fe , with a half life of 2.7 years, decays via electron capture to stable ^{55}Mn with the emission of Auger electrons and 5.89 keV X-rays. ^{63}Ni is an important radionuclide in safety analysis of nuclear waste repositories and ^{55}Fe is an important contributor to the radioactivity of nuclear waste in the first few years of storage. In this work, liquid scintillation counting was used for the determination of both radionuclides in spent ion-exchange resins taken from the water retreatment system of the IEA-R1 reactor and stored at the Radioactive Waste Management Laboratory of the Nuclear and Energy Research Institute (IPEN-CNEN/SP). Since nuclear waste usually contains many beta emitters, such as ^3H , ^{14}C , ^{60}Co , ^{90}Sr , and ^{137}Cs , a highly efficient chemical separation method is required to isolate ^{55}Fe and ^{63}Ni from all other radionuclides. Hydroxide precipitation was used to separate ^{55}Fe and ^{63}Ni from the waste matrix and ion exchange chromatography was used to separate ^{55}Fe and ^{63}Ni from each other as well as from interfering radionuclides. The chemical yield was above 90% for ^{63}Ni and above 60% for ^{55}Fe . The results of activity measurements correlated well with the concentration of ^{60}Co in this waste.

Keywords: radioactive waste, neutron activation, correlation factor.

1. INTRODUCTION

One of the most radioactive solid waste products of a reactor is a mixed-bed ion exchange resin that has been used for water purification in the refrigeration system. The activity of the radionuclides in packages of this waste must be known in order to meet the limits required by government agencies for its final disposal. Such limits include radionuclides that are long-lived alpha and beta emitters. In order to quantify them, radiochemical separation processes must be used. Measurement of these radionuclides involves high expenses and high doses of radiation. Because of this, factors are sought that relate the activities of these difficult-to-measure radionuclides with radionuclides that can be easily quantified by direct and external measurements of the packages.

^{55}Fe , ^{59}Ni and ^{63}Ni produced by activation of the reactor's structural metallic materials are among the radionuclides present in nuclear reactors; they are important in terms of activity and half life. These radionuclides are in a difficult-to-measure group and their measurement is only possible using radiochemical analysis or by correlation factors due to the absence of gamma emitters with significant intensities. For the radiochemical analyses, they are individually separated from the matrix and from other radionuclides present. ^{55}Fe decays to ^{55}Mn by means of electron capture, emitting Auger electrons or X-rays at the low energy level of 5.89 keV, and ^{63}Ni is a pure beta emitter with a maximum energy of 66.95 keV. The objective of this work was to measure ^{55}Fe and ^{63}Ni in ion exchange resin samples by the Liquid Scintillation method and calculate the ratio between the two radionuclides' activity with ^{60}Co in order to determine their correlation factor. The purification process utilized is based on a simultaneous method that combines hydroxide precipitation and purification with anionic resin and chromatographic resin impregnated with Dimethylglyoxime (DMG) as described by Hou (2005). Coprecipitation with hydroxides eliminates the main matrix components and the anionic resin separates ^{55}Fe from ^{63}Ni and the interfering radionuclides. Purification of ^{63}Ni is based on a traditional nickel analysis by means of precipitation with dimethylglyoxime. This analysis is simplified by using Ni-Eichrom resin that contains DMG adhered to the polymer pores, in which a Ni-DMG complex is formed.

2. MATERIALS AND METHODS

2.1 Equipment and reagents

For the radiometric measurements of ^{55}Fe and ^{63}Ni , a Hidex 300 SL model Canberra automated liquid scintillation counting system was used. The device used a triple photomultiplier tube that allowed for automatic calibration of sample radioactivity using the TDCR method (Triple to Double Coincidence Ratio); or through an external standard. Determination of stable Fe and Ni carriers were carried out by means of a Liberty RL sequential model inductively coupled plasma optical emission spectrometer (ICP-OES). The Perkin-Elmer Ultima Gold AB cocktail was used. ^{55}Fe and ^{63}Ni standard solutions were prepared and calibrated by the LNMRI at the Radioprotection and Dosimetry Institute, IRD. Dowex 1x4 anionic resin and Eichrom Ni resin and other analytical-grade chemical reagents were used in the process of separating and purifying the radionuclides.

2.2 Procedure

Approximately 1 gram of the sample was weighed that was dried in an oven at 70 °C for 24 hours in a beaker. 0.2 ml of 20 mgL⁻¹ Fe solution, 0.2 ml of 10 mgL⁻¹ Ni solution, 20 mL HNO₃ and 20 mL H₂O₂ were added. It was then heated on an electric hot plate until it had completely evaporated. Next, 10 mL HNO₃ and 2 mL HClO₄ were added. It was again evaporated and the salts were dissolved in 10 mL of 9 mol L⁻¹ HCl. It was transferred to a centrifuge tube in which 20 mL of water and 1 mol L⁻¹ NaOH were added until pH 9 when precipitation took place. The precipitate was separated by centrifuge and washed with 6 mol L⁻¹ NaOH and dissolved with 9 mol L⁻¹ HCl. The sample was percolated in a 15 cm long, 0.8 cm diameter column containing Dowex 1x4 anionic resin pretreated with 30 ml of 9 mol L⁻¹ HCl. It was washed with 20 ml of mol L⁻¹ HCl and the effluent and washing solution were reserved for Ni determination, since Ni isn't retained in the resin. The column was then percolated with 30 ml of 4 mol L⁻¹ HCl to remove the metals that form ionic complexes in concentrated HCl solution and retained in a column as shown by Hou (2005) and the effluent was discarded. The Fe was eluted with 30 ml of 0.5 mol L⁻¹ HCl, evaporated until it was dry, and the residue was dissolved with 2 ml of 1 mol L⁻¹ H₃PO₄ in order to decolor the solution of Fe⁺³ and thus diminish quenching due to color as proposed by Warwick (2006). 0.1 mL was taken for Fe analysis by ICP-OES to determine chemical recovery. 15 mL of the scintillation solution was added to the rest of the solution, and after it had rested in a refrigerator for 3 hours ⁵⁵Fe was counted in the scintillator for 30 minutes.

The effluent reserved from the previous step was evaporated until it was dry using an electric hot plate. The salts were dissolved with 1 mol L⁻¹ HCl. 1 ml of 1 mol L⁻¹ ammonium citrate was added and the pH was adjusted to 10-11 with NH₄OH. This solution was percolated in a column with Eichrom Ni resin that had been pre-treated with 5 ml of 0.2 mol L⁻¹ ammonium citrate adjusted to pH 10. Precipitation of Ni-DMG complex took place, which can be seen by a red band in the top of the column. The column was washed with 10 mL of 0.2 mol L⁻¹ ammonium citrate adjusted to pH 10 and was discarded. The Ni-DMG complex was eluted with 3 successive additions of 2 ml of 3 mol L⁻¹ HNO₃. It was evaporated at a low temperature until there was 1 mL of liquid. 5 mL of water was added and evaporated again to 1 mL. Finally, 2 mL of water was added and 0.1 mL was removed for stable Ni analysis by ICP-OES along with 15 mL of Ultima Gold AB cocktail. Counting was carried out after the solution had rested for three hours in refrigeration. The flowchart in figure 1 shows the summary of the analytical process.

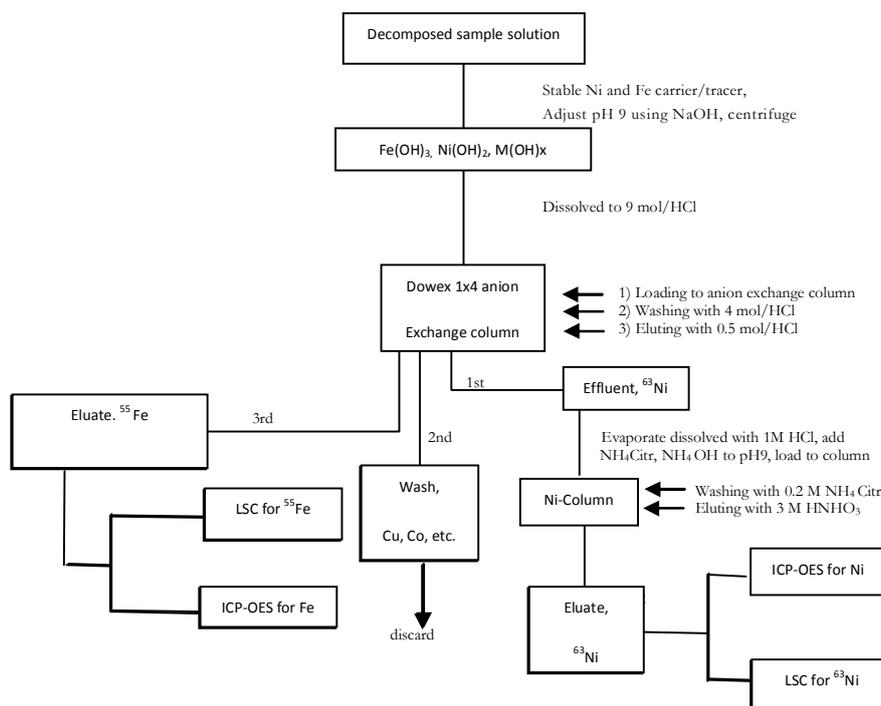


Figure 1. Chemical procedure for simultaneous ^{55}Fe and ^{63}Ni determination.

3. RESULTS AND DISCUSSION

In the dissolution process of the radionuclides in $9 \text{ mol L}^{-1} \text{ HCl}$ medium, other metals present such as Cs and Co also form anionic complexes in solution. These elements can be absorbed by the anionic column and interfere with the analysis. To evaluate this possible interference, the same activity of ^{60}Co and ^{137}Cs was added in a standard ^{63}Ni and ^{55}Fe solution and its separation began in the same manner as the sample. As in Hou (2005), it was verified that ^{63}Ni isn't retained and leaves in the effluent produced by washing with $9 \text{ mol L}^{-1} \text{ HCl}$ and that ^{60}Co and ^{137}Cs are eliminated in the second washing with $4 \text{ mol L}^{-1} \text{ HCl}$, leaving only Fe, which is eluted with $0.5 \text{ mol L}^{-1} \text{ HCl}$. The beta spectra presented in figure 2 show that analysis of these patterns added to the interferences is efficient in separating Fe from Ni.

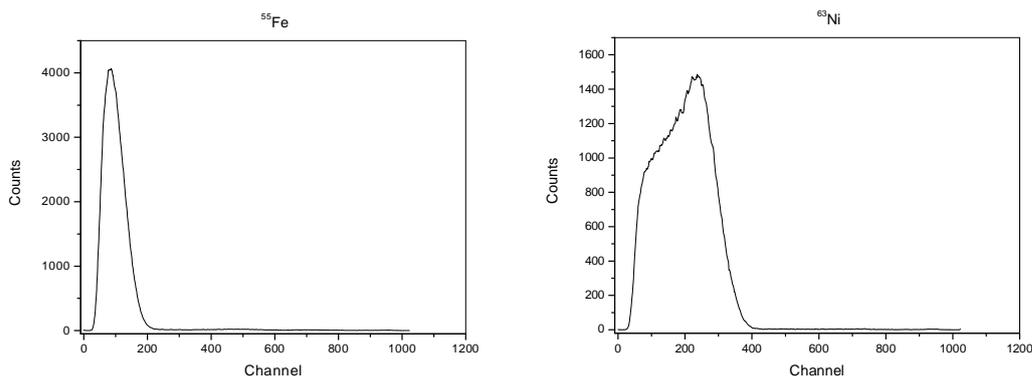


Figure 2. LSC spectra in mode.

The average ^{63}Ni and ^{55}Fe beta efficiencies from three results obtained with standard solutions added to the carriers and processed in the same manner as the samples were 70 and 37% respectively. Chemical recovery of carriers determined by ICP-OES oscillated between 0.70 and 0.90 for Ni and 0.50 and 0.95 for Fe.

The results obtained presented on table 1 show the distribution of ^{63}Ni and ^{55}Fe in the resin samples from the IEA-R1 reactor. Radioactivity was corrected for their input data in the IPEN waste deposit.

Table 1. Concentrations of ^{55}Fe and ^{63}Ni in spent resins samples from IEA-R1 reactor

Sample	1993		2003		
	^{55}Fe Bq/g	^{63}Ni Bq/g	Sample	^{55}Fe Bq/g	^{63}Ni Bq/g
RTI-06-T-03-I	1.79E+01	1.039E+02	RTI-27 T-10-I	2.54E+02	8.875E+03
RTI-07-T-03 -S2	3.29E+01	1.386E+02	RTI-28 T-11- I	3.53E+03	3.401E+03
RTI-08 T-03-S3	2.27E+02	1.564E+02	RTI-30 T-12- I	1.01E+03	2.853E+03
RTI-08 T-03-S4	2.68E+01	1.409E+02	RTI-35 T-14- I	8.13E+01	2.248E+03
RTI-09 T-03-S4	9.97E+01	1.552E+02	RTI-36 T-14-M	4.83E+02	2.970E+03
RTI-10 T-01-S1	2.22E+01	1.870E+02	RTI-40 T-16- I	7.44E+02	4.569E+03
RTI-11 T-01 -S2	2.30E+01	1.610E+01	RTI-41 T-16-M	1.33E+03	4.322E+03
RTI-12-01-S3	7.09E+01	2.018E+02			
RTI-13 -01 -S4	1.32E+02	2.292E+02			
RTI-14 -01 -S5	1.47E+02	2.424E+02			

As mentioned before, pure beta emitting radionuclides are hard to measure directly and destructive methods of the waste samples followed by radiochemical separation of the isotope of interest are necessary for their quantification. For this reason, functions are sought to be established that correlate the activity of these radionuclides with those that can be directly measured by gamma spectroscopy, mainly of ^{137}Cs and ^{60}Co . After correlations have been established, and when the activity of ^{137}Cs and ^{60}Co are known in the packaged waste, it is possible to indirectly calculate the activity of radionuclides that are difficult to measure, such as is the case of ^{63}Ni and ^{55}Fe .

Like cobalt, iron and nickel are present in the steel impregnated in the reactor and the interaction of the neutrons of these materials result in ^{60}Co as well as ^{55}Fe and ^{63}Ni . In a neutral aqueous medium, these elements also have similar behavior, and due to the similarity of production and transport it is expected that these radionuclides correlate well.

The weighted linear regression of the logarithm of the variables, the function of which is expressed as:

$$C_c = a \times C(k)^b \quad (1)$$

In which:

C_c is the activity of the critical radionuclide, or those that aren't measured directly and $C(k)$ is the activity of the directly measured radionuclides.

This can be represented by a line on the logarithmic scale:

$$y = A + B \cdot x \quad (2)$$

$$\text{with } y = \log c(c) \text{ and } x = \log c(k)$$

Weighted regression can be applied that takes into consideration the variables of precision of measurement of activities of x as well as y and the resolution of this type of adjustment results in an approximation whose origin slope and order values differ very little in the solution (Alcalá, 1997).

The correlation factors obtained were 0.989 for $^{63}\text{Ni}/^{60}\text{Co}$ and 0.685 for $^{55}\text{Fe}/^{60}\text{Co}$ in the samples of resins used in the reactor.

4. CONCLUSIONS

The combination of the coprecipitation method followed by purification utilizing anionic and chromatographic resins was efficient at separating these elements from the matrix and from each other. Utilization of the DMG chromatographic column resulted in a reduction of organic waste volume that had been previously used to separate Ni. Determination time is short because the sequential process. The interfering metals are eliminated during the process. Positive interference from ^{59}Ni has to be corrected for despite the values expect being quite small because of its very long half-life (7.6×10^4 years) compared to ^{63}Ni (100.1 years), therefore resulting in a very large $^{63}\text{Ni}/^{59}\text{Ni}$ ratio. This ratio in materials with 30 years of irradiation can be assumed to be 100 (Hou, 2005), showing that ^{59}Ni interference is insignificant. Due to the high level of selectiveness, the method could be used in the analysis of other solid waste, requiring only optimization of the dissolution process. Analysis speed allows the large number of samples needed to establish correlation factors in radioactive waste to be analyzed.

5. REFERENCES

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