RADIOCHEMICAL SEPARATION OF NICKEL FOR $^{59}$Ni and $^{63}$Ni
ACTIVITY DETERMINATION IN NUCLEAR WASTE SAMPLES

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ABSTRACT

A radiochemical separation scheme for nickel is presented in which the separation was performed by anion-exchange chromatography, extraction chromatography, using Ni resin, and precipitation techniques. Nickel was separated from uranium and iron by co-precipitation of them with ammonium hydroxide. Nickel was purified by Ni resin and the $^{63}$Ni was measured by liquid scintillation counting and the $^{59}$Ni by low energy gamma spectrometry. Samples of radioactive wastes such as evaporator concentrate, filter and resin were analysed. The ratios $^{59}$Ni/$^{63}$Ni determined for different samples are in the interval of 0.03-0.14. The chemical yield for separation procedure for Ni is determined with the addition of Ni (2 mg/L) as yield monitor and using ICPAES technique for Ni concentration measurements.

1. INTRODUCTION

For legal and regulatory purposes, the IAEA defines radioactive waste as waste that contains or is contaminated with radionuclides at concentrations or radioactivity levels greater than clearance levels as established by the regulatory body. The radioactive wastes are residues that have been produced and released to the environment by human nuclear activity and for which no future use is foreseen. In the case of wastes each country has its own classification, in general we can identify three types of wastes, that are, Low Level Waste (LLW), contain primarily short lived radionuclides which refer to half-lives shorter than or equal to 30-year half-life, Intermediate Level Waste (ILW), radioactive non-fuel waste, containing sufficient quantities of long-lived radionuclides that generally refers to half-lives greater than 30-year half-life. And a third one that is High Level Waste (HLW), arise from the reprocessing of spent fuel from nuclear power reactors to recover uranium and plutonium, containing fission products that are high radioactive, heat generating and long-lived. I would like to draw attention to the fact that the waste classification LLW, ILW, HLW used here is only one of several alternative schemes, we adopted the simplest of them. Identification and characterization of radioactive wastes is a technical challenge because of their importance in choosing the appropriate permanent storage mode or further processing.
The safety planning for disposal of LLW and ILW radioactive waste takes account in special long half-life radionuclides. Both $^{59}\text{Ni}$ and $^{63}\text{Ni}$ are activation products of stable nickel, which was present as an impurity in fuel cladding materials or the uranium fuel of reactors [1]. $^{59}\text{Ni}$ (half-life $7.6 \times 10^4$ years) is produced by neutron irradiation of $^{58}\text{Ni}$ and decays by electron capture to stable $^{59}\text{Co}$ with emission of 6.9 keV x-rays. $^{63}\text{Ni}$ (half-life 100 years) emits only low-energy beta rays with a maximum energy of 67 keV, and is produced through neutron irradiation of $^{62}\text{Ni}$. Counting requirements dictated that prior the measurement these isotopes should be separated and purified with the purpose of removing the radiometric and chemical interferent elements so that they are essentially free of significant radioactive contamination.

Xiaolin [2] proposed a analytical method for the determination of $^{63}\text{Ni}$ and $^{55}\text{Fe}$ in nuclear waste samples. Hydroxide precipitation was used to separate $^{63}\text{Ni}$ and $^{55}\text{Fe}$ from the interfering radionuclides as well as from each other. The separated $^{63}\text{Ni}$ was further purified by extraction chromatography. According to Hou the recovery of Fe and Ni by hydroxide precipitation using $\text{NH}_4\text{OH}$, was about 99.9% and 21.9%, respectively. Lee [3] proposed a sequential separation procedure developed for determination of $^{99}\text{Tc}$, $^{95}\text{Nb}$, $^{55}\text{Fe}$, $^{90}\text{Sr}$ and $^{59/63}\text{Ni}$ in various radioactive wastes. Ion exchange and extraction chromatography were adopted for individual separation of the radionuclides. According to Lee Ni separation on the cation-exchange resin column was not selective enough therefore a further purification of Ni was performed by precipitation with dimethylglyoxime.

The aim of this work is the sequential analysis of nuclear waste containing several radionuclides (Pu, U, Am, Sr, Fe e Ni) where the last step consists in the separation of U, Fe and Ni. Thus we established the procedure for sequential separation of Pu, Am, Sr [4] in which we also included one step that is the hydroxide precipitation to separate U and Fe of Ni once Ni remains in solution in the co-precipitation of U and Fe.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

All reagents used were analytical grade. The detection of radioactive $^{63}\text{Ni}$ was carried out by Liquid Scintillation Counting (LSC), using the Quantulus 1220 spectrometer, the vials used were the 20 mL polyethylene and the scintillation cocktail was the Optiphase Hisafe 3, all from PerKinElmer Inc. (PerkinElmer Inc., Finland). The column materials used in the analysis were Ni Resin in pre-packed 2 mL columns, 100-150 µ particle size, an extraction chromatographic material available from Eichrom Technologies (USA) and the anion exchange resin Dowex 1x8, Cl⁻ form, from Sigma-Aldrich Chemical Co., (USA). $^{59}\text{Ni}$ was analyzed using Ultra-LEGe Detector (GUL) with a cryostat window of Beryllium low energy $\gamma$-detector containing a active area of 100 mm², efficiency 5.9 keV for $^{55}\text{Fe}$ with a resolution of 160 eV FWHM, from Camberra (USA). The recovery was obtained analyzing stable nickel by ICP-AES.
2.2. Separation and Purification of Nickel

The sequential determination is based on radiochemical procedure that consists of three steps performed by anion-exchange chromatography, extraction chromatography, using Eichrom resins, and precipitation techniques. For each aliquot was added 2 mL of Ni (2mg/mL), 1 mL of Sr (5 mg/mL) and 2 mL of Fe (3 mg/mL) as carriers and yield monitor. In the first step, the separation of Pu by ion exchange chromatography, anion exchange column (Dowex 1x8, Cl-form. 100-200 mesh, Sigma Chemical Co. USA), is based on the formation of anionic complexes of Pu(IV) with NO$_3^-$ or Cl$^-$ in concentrated HNO$_3$ or HCl. In the second one the effluent from the anion exchange column was used to separate Am and Sr by co-precipitation with oxalic acid of U, Fe and Ni that remains in the filtrate.

In the third step we use the filtrate to separate Ni of U and Fe [2,4]. The filtrate was heated to dryness and the solid obtained was dissolved in 30 mL of concentrate nitric acid and heated to dryness in order to destroy the excess of oxalic acid. The solid obtained was hot dissolved in 30 mL of 3:2 nitric acid and was diluted to 200 mL with deionized water. The pH of the solution was corrected to 9.0 with ammonia hydroxide for co-precipitation of iron hydroxide and uranium.

After filtration, the filtrate was heated to dryness and retaken with 20 mL of HCl concentrate and again heated to dryness. The solid obtained was dissolved in 25 mL of 1M HCl and was added 1 mL of ammonium citrate to the sample being the pH adjusted to 8-9 with ammonium hydroxide [5]. A nickel resin extraction chromatography column (Eichrom Industries Inc. USA) was pre-conditioned with 5 mL of solution 0.2M ammonium citrate that has been adjusted to pH 8-9 with ammonium hydroxide (Eichrom Technology Inc – Analytical Procedures). The column was loaded with the sample and rinsed with 20 mL of solution 0.2M ammonium citrate. Nickel was eluted with 10 mL of solution 3M HNO$_3$.

2.3. Determination of $^{63}$Ni by LSC

From the 10 mL of solution 3M HNO$_3$ eluted of the column, it was taken an aliquot of 3 mL collected in a scintillation vial. It was added 17 mL of the scintillation cocktail and the vial was shaken vigorously. Before counting, in order of minimizing luminescence interferences, the vial was storaged in the dark for 24 hours.

In order to calibrate the counter and to determine the counting conditions, it was prepared a $^{63}$Ni standard solution and a blank solution, in the same conditions of the sample. The counting conditions set-up was a time of counting of 60 minutes and a channel interval of 50-400.
3. RESULTS AND DISCUSSION

In the analysis by LSC the following parameters were determined. The counting efficiency was obtained by the Equation 1.

\[
Eff = \frac{R_{st} - R_b}{A_{st} \cdot 60 \cdot Y}
\]  

(1)

where \(R_{st}\) is the count rate in counts per minute (cpm) of the \(^{63}\)Ni standard, \(R_b\) is the cpm of the blank, \(Y\) is the chemical yield and \(A_{st}\) is the activity of the standard (in Bq). The counting efficiency obtained was 71.5 %, with a background of 12.5 ± 1.76 cpm. If we compare with the values determined by Xiaolin [2], that is, a counting efficiency of 71.2 % and a background of 1.30 cpm to 30 minutes of counting, in samples of graphite and concrete, it is observed the same efficiency, however, with a background increased.

The sample activity was obtained by the Equation 2.

\[
A = \frac{R_s - R_b} {Eff \cdot Y \cdot Q \cdot 60}
\]  

(2)

where \(R_s\) is the count rate (cpm) of the sample and \(Q\) is the quantity of sample.

The limit of detection was calculated using the formula proposed by Currie 1968, Equation 3, where \(L_d\) is the limit of detection with 95 % at confidence level.

\[
L_d = \frac{2.71 + 3.29 \sqrt{t \cdot R_b}}{60 \cdot t \cdot Eff \cdot Q}
\]  

(3)

Xiaolin [6] related background count rates from 3-10 cpm to LSC mean while the background obtained by us was 12.5 cpm. The \(L_d\) obtained was 12.0 Bq/L, and this relatively high value results from the high background count rate.

The Figure 1 shows a typical spectrum of \(^{63}\)Ni for a sample of evaporator concentrate. The chemical yield was 58 % determined by measuring the stable Ni added as carrier using ICP-AES. This value is also used for the calculations of activities of \(^{59}\)Ni.

The results obtained by LSC, using the parameters as set up, and that obtained by low energy \(\gamma\) detection for activities of \(^{63}\)Ni and \(^{59}\)Ni, respectively, are shown in the Table 1. Every measurement was considered along with a confidence interval, the uncertainty to the measurement.
Fig. 1. Spectrum of $^{63}\text{Ni}$ in a sample of evaporator concentrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{63}\text{Ni}$ (Bq g$^{-1}$)</th>
<th>$^{59}\text{Ni}$ (Bq g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator concentrate</td>
<td>31±2</td>
<td>0.86 ± 0.04</td>
</tr>
<tr>
<td>Ion-exchange Resin</td>
<td>1.48 ± 0.07 x 10$^4$</td>
<td>2.2 ± 0.1 x 10$^3$</td>
</tr>
<tr>
<td>Filter</td>
<td>5.4 ± 0.3 x 10$^3$</td>
<td>2.1 ± 0.2 x 10$^2$</td>
</tr>
</tbody>
</table>

Due to the very long half-life of $^{59}\text{Ni}$ its radioactivity in radioactive waste samples is normally much lower than $^{63}\text{Ni}$ [2]. This was comprovied by the values obtained for both radioisotopes to the same sample, in the Table 1. According to Scheuerer [7] the ratio of activity concentrations of $^{59}\text{Ni}$ to $^{63}\text{Ni}$ is about 0.008 for environmental samples, steel and concrete. For the samples of nuclear waste analysed by our laboratory the ratio found varied from 0.03 to 0.14, these values indicate that the concentration activities for $^{59}\text{Ni}$ are yet bigger than that for $^{59}\text{Ni}$. We can, therefore, consider that these ratios are in accordance with that ratio waited for $^{59}\text{Ni}$/$^{63}\text{Ni}$.

4. CONCLUSION

An analytical procedure for determination of nickel in nuclear waste samples was developed. The separation of various radionuclides was perfomed and the use of ammonium hydroxide for separation of nickel from uranium and iron occurred according was proposed. Radionuclides $^{63}\text{Ni}$ and $^{59}\text{Ni}$ were determined by LSC and low gamma energy spectrometry after be purified by Ni resin. The ratio $^{59}\text{Ni}$/$^{63}\text{Ni}$ fell within a range that indicates a higher activity of $^{63}\text{Ni}$, which was to be expected in view of the difference between the half-lives of radionuclides.
5. ACKNOWLEDGMENTS

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6. REFERENCES