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# Radiochemical Separation of Nickel for $^{59}\text{Ni}$ and $^{63}\text{Ni}$ Activity Determination in Nuclear Waste Samples

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## 1. Introduction

For legal and regulatory purposes, the International Atomic Energy Agency (IAEA, 1994) 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 by human nuclear activity and for which no future use is foreseen. Besides the nuclear power plants, the nuclear weapons testing, medical uses and various research studies involve a large number of radionuclides. In particular the nuclear accidents such as Three Mile Island Nuclear Power Station, where some gas and water were vented to the environment around the reactor, Chernobyl Nuclear Power Plant, the effects of the disaster were very widespread and Fukushima II Nuclear Power Plant have also released a large amount of radionuclides to environment.

In the case of radioactive wastes each country has its own classification, in general we can identify three types of wastes, that are, Low Level Waste (LLW), the LLW wastes 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 which refer to half-lives greater than 30 years. 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. We would like to call attention to the fact that the waste classification LLW, ILW, HLW used here is only one of several alternative schemes; we adopted the simplest one.

Identification and characterization of radioactive wastes is a technical challenge because of their importance in choosing the appropriate permanent storage mode or further processing. Characterization definition of nuclear waste by IAEA (IAEA, 2003) is "the determination of the physical, chemical and radiological properties of the waste to establish the need for further adjustment, treatment, conditioning, or its suitability for further handling, processing, storage or disposal. Thus, it involves a collection of data that pertains to specific waste properties as well as processing parameters and quality assurance, some of

which include the following: thermal, mechanical, physical, biological, chemical and radioactivity properties (IAEA, 2007).

Testing and analyzes to demonstrate the radioactive content and the quality of final waste forms and waste packages are key components of this knowledge and control and are essential to accurate characterization of the waste. Physical characterization involves inspection of the waste to determine its physical state (solid, liquid or gaseous), size and weight, compactability, volatility and solubility, including closed waste packages which can be done using a variety of techniques, such as radiography (X-ray). Chemical waste characterization involves the determination of the chemical components and properties of the waste that is, potential chemical hazard, corrosion resistance, organic content, reactivity. This is most often done by chemical analysis of a waste sample. The radioactive inventory of various materials needs to be assessed for the classification of the nuclear waste. Radiological waste characterization involves detecting the presence of individual radionuclides and its properties such as half-life, intensity of penetrating radiation, activity and concentration and quantifying their inventories in the waste. This can be done by a variety of techniques, such as radiometric methods, mass spectrometric methods depending on the waste form, radionuclides involved and level of detail/accuracy required.

Furthermore, for developing a scaling factor (IAEA, 2009) to be applicable to the assessment of the radioactive inventory of the wastes with various matrices, it is indispensable to prepare a database compiled with a large numbers of information related to the radioactive inventory of long lived alpha and beta emitting nuclides which are difficult to measure (DTM) and gamma emitting nuclides which are easy to measure (ETM). It is necessary to develop analytical techniques for the DTM nuclides.

The aim of this work was to develop a sensitive analytical procedure for simultaneous determination of radionuclides difficult to measure. Between them is the  $^{59}\text{Ni}$  and  $^{63}\text{Ni}$  determination in low and intermediate level wastes from Brazilian Nuclear Power Plants – Eletrobrás Termonuclear according to an analytical protocol developed based on sequential separation of different radionuclides presents in the waste matrices (Reis et al, 2011). Sources for  $^{59}\text{Ni}$  are austenitic steel in the reactor and activation of nickel dissolved in the coolant and in corrosion particles deposited on the core. The content of nickel in stainless steel is around to 10% and in Inconel in the range of 50–75%. Furthermore, nickel is found as an impurity in Zircaloy, ~ 40 ppm, and in reactor fuel, ~ 20 ppm (Lingren et al, 2007).

## 2. The radiometric detection and techniques for $^{59}\text{Ni}$ and $^{63}\text{Ni}$

Radioactive wastes are residues with different radionuclide compositions, placing, therefore considerable demands by measurement techniques used in their characterization. All radioisotopes, at some stage, require quantitation of the isotope, which is done by measuring the intensity of radiation emitted for the three main types of ionizing radiation. Radioactive isotopes of elements are normally determined by their characteristic radiation, i. e., by radiometric methods. Radiometric determination is performed by instrumental analysis using sophisticated methods such as liquid scintillation counters that allow beta spectrometry, alpha spectrometry with semiconductor detectors and high resolution gamma spectrometry for high and low energy gamma emitting nuclides. Besides, mass

spectrometric methods can be also used for the determination of radionuclides once they are normally used for determination of isotopes of elements.

There are several types of detectors that can be used for the measurement of ionizing radiation. In the specific case of  $^{59}\text{Ni}$  and  $^{63}\text{Ni}$ , the more common radiation detection systems are ultra low energy gamma detection and liquid scintillation detection on the basis of charge carriers (holes and electrons) and liquid scintillation phenomena, respectively. Furthermore, for sequential analysis of these radionuclides alpha spectrometry can be applied to alpha emitters associated and presents in ILW and LLW samples.

## 2.1 The semiconductors detectors

The most recent class of detector developed is the *solid-state semiconductor detector*. In these detectors, radiation is measured by means of the number of charge carriers set free in the detector, which is arranged between two electrodes. Ionizing radiation produces free electrons and holes. The number of electron-hole pairs is proportional to the energy transmitted by the radiation to the semiconductor. As a result, a number of electrons are transferred from the valence band to the conduction band, and an equal number of holes are created in the valence band. Under the influence of an electric field, electrons and holes travel to the electrodes, where they result in a pulse that can be measured in an outer circuit. Solid state detectors are fabricated from a variety of materials including: germanium, silicon, cadmium telluride, mercuric iodide, and cadmium zinc telluride.

Germanium detectors are mostly used for spectrometry in nuclear physics and chemistry. The Ultra Low Energy Germanium (Ultra-LEGe) detectors extends the performance range of germanium detectors down to a few hundred electron volts, providing resolution, peak shape, and peak-to-background ratios once thought to be unattainable with semiconductor detectors. According to its specification this detector offers excellent performance over a wide range of detector sizes. The resolution, for example, of a 100 mm<sup>2</sup> Ultra-LEGe is less than 150 eV in terms of full-width-half-maximum (FWHM) at 5.9 keV.

Radionuclides commonly emit gamma rays in the energy range from a few keV to ~10 MeV, corresponding to the typical energy levels in nuclei with reasonably long lifetimes. The boundary between gamma rays and X rays is somewhat blurred, as X rays typically refer to the high energy electromagnetic emission of atoms, which may extend to over 100 keV, whereas the lowest energy emissions of nuclei are typically termed gamma rays, even though their energies may be below 20 keV. Therefore,  $^{59}\text{Ni}$  that decays by electron capture with emission of 6.9 keV X-rays is suitable to be detected by low energy gamma spectroscopy using Ultra Low Energy Germanium detectors.

## 2.2 The liquid scintillation counting

Beta emitting radionuclides are normally measured by a gas ionization detector or liquid scintillation counting (LSC). In LSC the scintillation takes place in a solution, the cocktails contain two basic components, the solvent and the scintillator(s). This allows close contact between the isotope atoms and the scintillator what becomes an advantage in measuring low-energy electron emitters due to the absence of attenuation. Once the solvent must act as an efficient collector of energy, and it must conduct that energy to the scintillator molecules

instead of dissipating the energy by some other mechanism (National Diagnostics, 2004). Liquid scintillation cocktails absorb the energy emitted by radioisotopes and re-emit it as flashes of light. A  $\beta$  particle, passing through a scintillation cocktail, leaves a trail of energized solvent molecules. These excited solvent molecules transfer their energy to scintillator molecules, which give off light. With LSC the short path length of soft  $\beta$  emissions is not an obstacle to detection. LSC can thus be used for the measurement of both high and low energy emitters.

A pulse height spectrum is a representation of the average kinetic energy associated with the decay of a particular isotope. When an isotope decays it liberates an electron or beta particle and a neutrino that have the energy associated shared between the two particles. As a result of that the resulting beta particles have a continuous distribution of energies from 0 to maximum decay energy ( $E_{\max}$ ). The amount of light energy given off is proportional to the amount of energy associated with the beta particle. Therefore, the beta decay shows a continuous energy distribution and beta particle spectrometry becomes an analytical technique in which it is difficult to identify individual contributions in the spectrum beta. The determination of various beta emitters such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{63}\text{Ni}$ ,  $^{55}\text{Fe}$ ,  $^{90}\text{Sr}$  requires chemical separation of the individual radionuclides from the matrix and from the other radionuclides before counting.

The isotope  $^{63}\text{Ni}$  is an artificial radionuclide. It is a pure  $\beta$  emitter with a half-life of 100 years. The maximum energy of the emitted  $\beta$ -radiation is 67 keV. No  $\gamma$  radiation is observed. Except  $^{59}\text{Ni}$  with a half-life of  $7.6 \times 10^4$  years all nickel radionuclides have very short half-lives. They range between 18 seconds and 54.6 hours. Therefore they don't disturb a measurement of  $^{63}\text{Ni}$ . Besides, LSC has a high counting efficiency for  $^{63}\text{Ni}$ , about 70%, i. e., the ratio cpm/dpm, counts per minute to disintegration per minute expressed as a percentage, in other words, the percentage of emission events that produce a detectable pulse of photons, making the technique widely used for the determination of  $^{63}\text{Ni}$ .

### 2.3 The alpha spectrometry

The sequential analyses determine in addition to  $^{59}\text{Ni}$  and  $^{63}\text{Ni}$  others DTM's present in the nuclear waste including alpha emitters. Therefore, alpha spectrometry is one complementary technique for the nuclear waste characterization either ILW or LLW.

In this technique to achieve results with good quality, the sample must be converted into a chemically isolated, thin layered and uniform source. The preparation of an alpha sample contains three basic steps: preliminary treatment, chemical separation and source preparation

Alpha-emitting radioisotopes spontaneously produce alpha particles at characteristic energies usually between about 4 and 6 MeV. Alpha particles (or  $^4\text{He}$  nuclei) are heavy charged, large and slow particles and loses some of its energy each time it produces an ion (its positive charge pulls electrons away from atoms in its path), finally acquiring two electrons from an atom at the end of its path to become a complete helium atom. These attenuation characteristics, which manifest themselves both within the sample and with any materials between the sample and the active detector volume, cause a characteristic tailing in the alpha peak. When tailing occurs (it is also called "spill down"), the accuracy with



which the peak areas can be determined is compromised because the peaks tend to have an asymmetric shape rather than the Gaussian shape.

The alpha particle energies of many isotopes differ by as little as 10 to 20 keV (Canberra, n.d.). The relatively small difference in alpha particle energy between some alpha emitters makes it difficult to spectrometrically separate the peaks once this is near the resolution of the silicon detectors used in alpha spectrometers. If two of these alpha particle energies are so close, they cannot be spectrometrically separated and if they are chemically the same, they cannot be chemically separated and analyzed.

Resolution is the ability of the spectrometry system to differentiate between two different alpha particles and its quantitative measure is the FWHM. Besides, a FWHM of about 15 keV can be achieved with electroplated sources because they have very little mass to slow down the alpha particles. For this reason it is essential that a thin source to be prepared in alpha spectrometry.

### 3. Radiochemical for radionuclides difficult to measure

#### 3.1 Radiochemical separation

The methods for separating, collecting, and detecting radionuclides are similar to ordinary analytical procedures and employ many of the chemical and physical principles that apply to their nonradioactive isotopes. One of the differences is interesting from the viewpoint of methodology. Substance separation in analytical chemistry in the majority of cases is not an end in itself. In radiochemistry, separation is most often an end in itself, for example, when a radionuclide is purified of other radioactive elements (Zolotov, 2005). Techniques used for separation include co-precipitation, liquid-liquid extraction, ion exchange and extraction chromatography. In some cases, two or more of these techniques are combined.

In order to account for the inevitable loss of the sample during separation, a specific isotope or tracer is added to the sample. A tracer represents the addition to an aliquot of sample a known quantity of a radioactive isotope that is different from that of the isotope of interest but expected to behave in the same way. Sample results are normally corrected based on tracer recovery. The percent of tracer lost in the chemical processes is equal to the percent of sample lost, assuming the tracer is homogeneously mixed with the sample and is brought into chemical equilibrium with the sample. Radiochemical analysis frequently requires the radiochemist to separate and determine radionuclides that are present at extremely small quantities. The amount can be in the picomole range or less, at concentrations in the order of  $10^{-15}$  to  $10^{-11}$  molar (United States Environmental Protection Agency, 2004). The use of a material that is different in isotopic make-up to the analyte and that raises the effective concentration of the material to the macro level is referred to as a carrier, a substance that has a similar crystalline structure that can incorporate the desired element.

Radiochemical waste characterization is the identification of radionuclides contained in a package of nuclear waste and the determination of their concentration. The problem the waste producers have to cope with comes from the fact that those nuclides which are mainly (pure)  $\beta$ - or  $\alpha$ -emitters cannot be measured by direct methods such as  $\gamma$ -scanning. In the waste packages produced by a nuclear power reactor the radionuclides may be originated as fission products from the nuclear fuel, activation products and transmutation nuclides, Table 1.

Products	Radionuclides	Decay mode
Fission products from the nuclear fuel	$^{90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{137}\text{Cs}$ , $^{129}\text{I}$ $^{134}\text{Cs}$	$\beta$ $\gamma$
activation	$^3\text{H}$ , $^{14}\text{C}$ , $^{94}\text{Nb}$ , $^{60}\text{Co}$ , $^{63}\text{Ni}$ , $^{54}\text{Mn}$ $^{55}\text{Fe}$ , $^{59}\text{Ni}$	$\beta$ EC
Transmutation nuclides	$^{241}\text{Am}$ , $^{242}\text{Cm}$ , $^{244}\text{Cm}$ , $^{235}\text{U}$ , $^{238}\text{U}$ and $^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$ $^{241}\text{Pu}$	$\alpha$ $\beta$

Table 1. Radionuclides obtained as products of nuclear power plants and their origin

Identification of these nuclides requires methods that, in general, involve analyses of waste samples using complex chemical analysis to separate the various radionuclides for measurement. Among the various proposed methods there are those who seek the identification of a radionuclide isolated or those seeking to identify by simultaneous determination two or more radionuclides in the same analysis.

The main constraint for a new protocol is to obtain a high recovery yield, a high-energy resolution and low interferences of other radionuclides. Thus, it is necessary to develop accurate and reliable methods for the determination of radionuclides in the low and intermediate radioactive samples. A simultaneous determination procedure was developed for the separation of Pu isotopes,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ ,  $^{244}\text{Cm}$ ,  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  using precipitation by oxalate, ion exchange resin, extraction of plutonium by TTA (thenoyltrifluoro acetone/benzene) and Sr by precipitation techniques. This method was applied for determination of these radionuclides in the grass, collected near Munich after the fallout from the nuclear accident at Chernobyl (Bunzl & Kracke, 1990). In another case, Pu, Am and Cm were determined by extraction chromatography using an organophosphorus compound immobilized on an inert support commercially available under the name TRU Resin (for Transuranium specific) from Eichrom Technologies, Inc. This method was used in samples from nuclear power plants such as spent ion exchange resins and evaporator concentrates (Rodriguez et al., 1997). Besides, combined procedure was used for the determination of  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$  and Pu isotopes by anion exchange for Pu isotopes analysis, the selective method for Sr isolation based on extraction chromatography using Sr Resin and the TRU Resin for separation of Am (Moreno et al., 1997). In the radiological characterization of low- and intermediate-level radioactive wastes the separation of Pu isotopes,  $^{241}\text{Am}$ ,  $^{237}\text{Np}$  and  $^{90}\text{Sr}$  was performed by anion-exchange chromatography, extraction chromatography, using TRU and Sr Resin, and precipitation techniques (Tavcar et al., 2007).

3.2 Combined procedure for Ni radionuclides separation

An analytical procedure for radiochemical characterization of radioactive waste material containing some of the radionuclides cited in Table 1 was developed. Radionuclides  $^{242}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{239} + ^{240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  were determined by alpha spectrometry whilst  $^{241}\text{Pu}$ ,  $^{90}\text{Sr}$ ,  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  were determined by LSC and  $^{59}\text{Ni}$  by low energy gamma spectrometry.  $^{242}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{243}\text{Am}$  and  $^{232}\text{U}$  were used as tracers and Sr (2 mg/mL), Fe (3 mg/mL) and Ni (2 mg/mL) were used as carriers. In this work was developed a sensitive method for sequential analyses of the radionuclides in samples of radioactive waste. The samples

analyzed were evaporator concentrate, resin and filter originated from Brazilian Nuclear Power Plants located at Angra dos Reis city (Reis et al, 2011).

The radiochemical procedure consists of three steps performed by anion-exchange chromatography, precipitation techniques and extraction chromatography, using TRU, Sr and Ni resins. In the first step, it was made the separation of  $^{242}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{239} + ^{240}\text{Pu}$  and  $^{241}\text{Pu}$  of the matrix by ion exchange chromatography using an anion exchange column (Dowex 1X8, Cl-form, 100-200 mesh, Sigma Chemical Co., USA). The separation is based on the formation of anionic complexes of Pu (IV) with  $\text{NO}_3^-$  or  $\text{Cl}^-$  in concentrated  $\text{HNO}_3$  or  $\text{HCl}$ . In the second one, the effluent from the exchange column was used to separate Am and Sr by co-precipitation with oxalic acid of Fe, U and Ni that are retained in the filtrate. Americium and Sr isolation was done using commercially available resins, TRU resin and Sr Resin, respectively. These resins can be used for a number of analytical purposes, including the separation of actinides as a group from the matrix, separation of Sr from the matrix and sequential separation of individual actinides and Sr. In the third step Ni was separated by co-precipitation of Fe and U. And after that, Fe and U were separated by ion exchange chromatography using the anion exchange column (Dowex 1X8, Cl form, and 100-200 mesh) and Ni was isolated by Ni Resin extraction chromatography column from Eichrom Technologies, Inc. This work represents a fundamental step in establishing an analytical protocol for radioactive waste management system.

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 (Kaye et al., 1994).  $^{59}\text{Ni}$  (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.

Hou (Hou et al., 2005) proposed an 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 him the recovery of Fe and Ni by hydroxide precipitation using  $\text{NH}_4\text{OH}$ , was about 99, 9% and 21, 9%, respectively. Lee (Lee et al., 2007) proposed a sequential separation procedure developed for determination of  $^{99}\text{Tc}$ ,  $^{94}\text{Nb}$ ,  $^{55}\text{Fe}$ ,  $^{90}\text{Sr}$  and  $^{59/63}\text{Ni}$  in various radioactive wastes. Ion exchange and extraction chromatography were adopted for the individual separation of the radionuclides. According to him 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 (Reis et al., 2011) in which we also included one step that is the hydroxide precipitation to separate U and Fe from Ni because Ni remains in solution in the co-precipitation of U and Fe.



### 3.3 Experimental

#### 3.3.1 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  $\mu$  particle size, an extraction chromatographic material available from Eichrom Technologies (USA) and the anion exchange resin Dowex 1x8,  $\text{Cl}^-$  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 an active area of 100  $\text{mm}^2$ , efficiency 5.9 keV for  $^{55}\text{Fe}$  with a resolution of 160 eV in terms of FWHM, from Canberra (USA). The recovery was obtained analyzing stable nickel by ICP-AES.

#### 3.3.2 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 ( $0.01 \text{ mol L}^{-1}$ ), 1 mL of Sr ( $0.02 \text{ mol L}^{-1}$ ) and 2 mL of Fe ( $0.01 \text{ mol L}^{-1}$ ) as carriers and yield monitor. In the first step, the separation of Pu by ion exchange chromatography, anion exchange column (Dowex 1x8,  $\text{Cl}^-$ -form. 100-200 mesh, Sigma Chemical Co. USA), is based on the formation of anionic complexes of the Pu(IV) with  $\text{NO}_3^-$  or  $\text{Cl}^-$  in concentrated  $\text{HNO}_3$  or  $\text{HCl}$ . 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 from U and Fe. 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 while Ni forms a soluble  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  complex.

After filtration, the filtrate was heated to dryness and retaken with 20 mL of  $\text{HCl}$  concentrate and again heated to dryness. The solid obtained was dissolved in 25 mL of  $1 \text{ mol L}^{-1}$   $\text{HCl}$  and was added 1 mL of ammonium citrate to the sample being the pH adjusted to 8-9 with ammonium hydroxide (Eichrom Technologies, 2003). A nickel resin extraction chromatography column (Eichrom Industries Inc. USA) was pre-conditioned with 5 mL of solution  $0.2 \text{ mol L}^{-1}$  ammonium citrate that has been adjusted to pH 8-9 with ammonium hydroxide. The column was loaded with the sample and rinsed with 20 mL of solution  $0.2 \text{ mol L}^{-1}$  ammonium citrate. Nickel was eluted with 10 mL of solution  $3 \text{ mol L}^{-1}$   $\text{HNO}_3$ . Figure 1 represents the flowchart for sequential separation of radionuclides in a sample of radioactive waste.

#### 3.3.3 Determination of $^{59}\text{Ni}$ by ultra low energy germanium detection

It was taken an aliquot of 3 mL from the 10 mL solution  $3 \text{ mol L}^{-1}$   $\text{HNO}_3$  eluted of the column. Measurements of  $^{59}\text{Ni}$  were performed with Ultra-LEGe Detector (GUL) with a

cryostat window of Beryllium low energy  $\gamma$ -detector containing an active area of 100 mm<sup>2</sup>, and resolution less than 150 eV (FWHM) at 5.9 keV, from Canberra Industries (USA).

### 3.3.4 Determination of $^{63}\text{Ni}$ by LSC

It was taken an aliquot of 3 mL collected in a scintillation vial from the 10 mL solution 3 mol L<sup>-1</sup> HNO<sub>3</sub> eluted of the column,. 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 stored in the dark for 24 hours.

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

### 3.4 Results and discussion

In the  $^{63}\text{Ni}$  analysis by LSC the following parameters were determined. The counting efficiency was obtained by the Equation 1.

$$Eff = \frac{R_{st} - R_b}{A_{st} \cdot 60 \cdot Y} \quad (1)$$

where  $R_{st}$  is the count rate in counts per minute (cpm) of the  $^{63}\text{Ni}$  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  $12.5 \pm 1.76$  cpm. If we compare with the values determined by Hou (Hou et al., 2005), 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.

$$A = \frac{R_s - R_b}{Eff \cdot Y \cdot Q \cdot 60} \quad (2)$$

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

The detection limit was calculated using the equation proposed by Currie (Currie, 1968) and according to Standard Methods (Standard Methods, 2005), Equation 3, where it is the total counting time for the blank and  $L_d$  is the limit of detection with 95 % at confidence level. The 95% confidence level means that, for a large number of observations, 95% of the observations indicate the presence of the analyte, whereas 5% of these observations reflect only random fluctuations in background intensity.

$$L_d = \frac{2.71 + 3.29\sqrt{t \cdot R_b}}{60 \cdot t \cdot Eff \cdot Q} \quad (3)$$

In the  $^{59}\text{Ni}$  analysis by ultra low energy gamma spectrometry the corresponding gamma peak area (6.3 keV) was correlated with the gamma peak area (5.9 keV) of  $^{55}\text{Fe}$ , taking

account the efficiency curve of the detector. The activities were related with the nominal activity of <sup>55</sup>Fe standard solution. The Figures 2 and 3 show typical <sup>59</sup>Ni spectra of evaporator concentrate and resin samples.

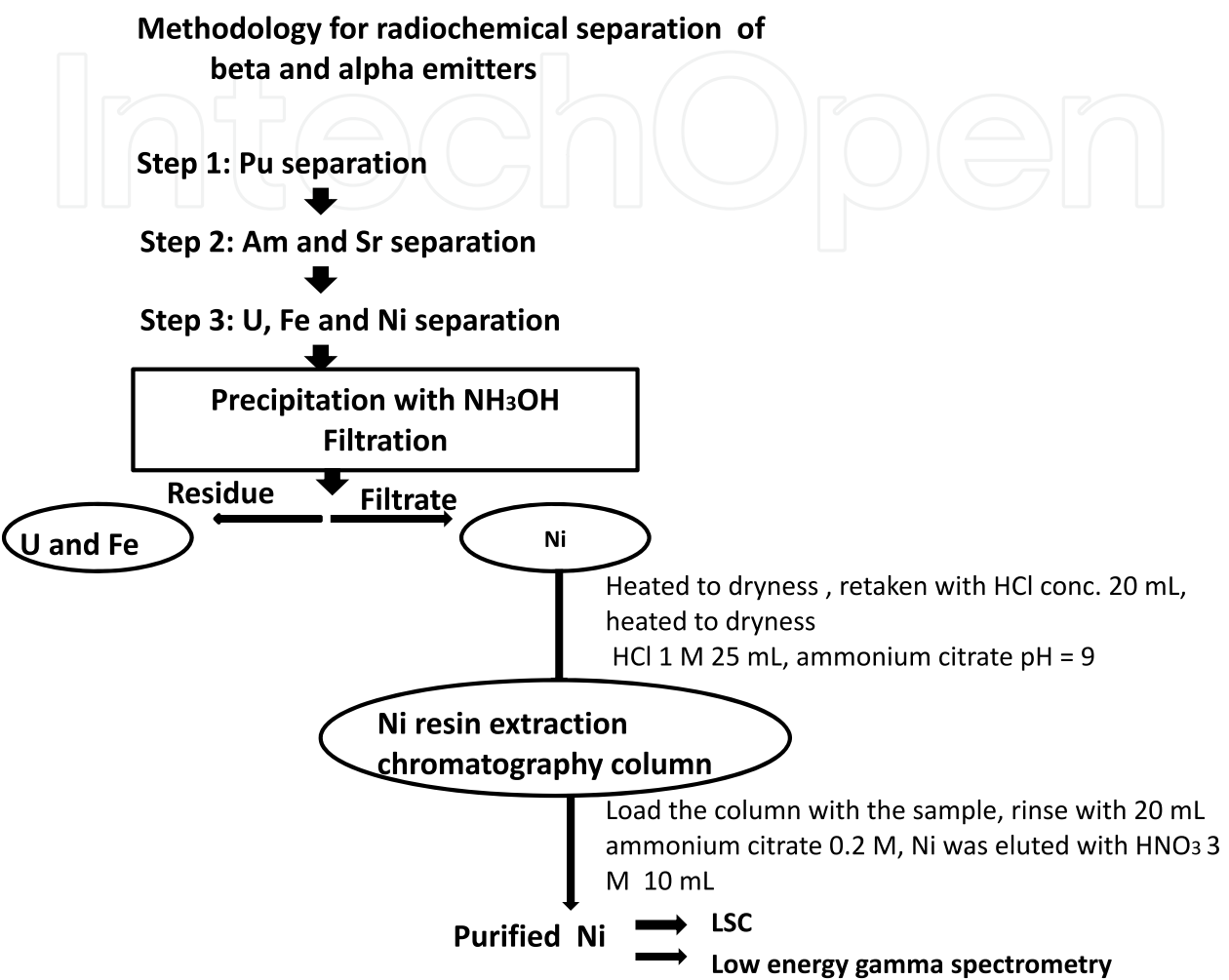


Fig. 1. Flowchart for radiochemical separation and purification of Nickel

Hou (Hou & Ross, 2008) 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 4 shows a LSC spectrum for an evaporator concentrate sample according to the parameters as were established.

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 <sup>59</sup>Ni.

The results obtained by LSC, using the parameters as set up, and that obtained by low energy  $\gamma$  detection for activities of <sup>63</sup>Ni and <sup>59</sup>Ni, respectively, are shown in the Table 2. Every measurement presented in Table 2 was considered along with a confidence interval, the uncertainty to the measurement.

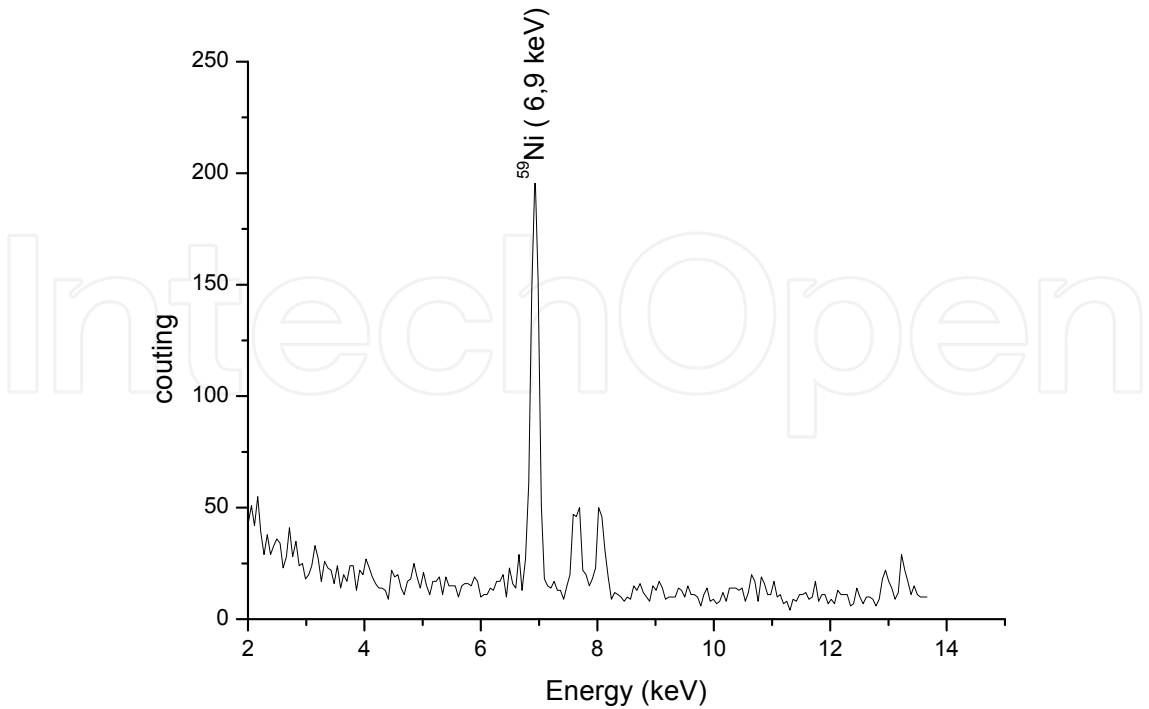


Fig. 2.  $^{59}\text{Ni}$  spectrum for a radioactive waste concentrate evaporator sample

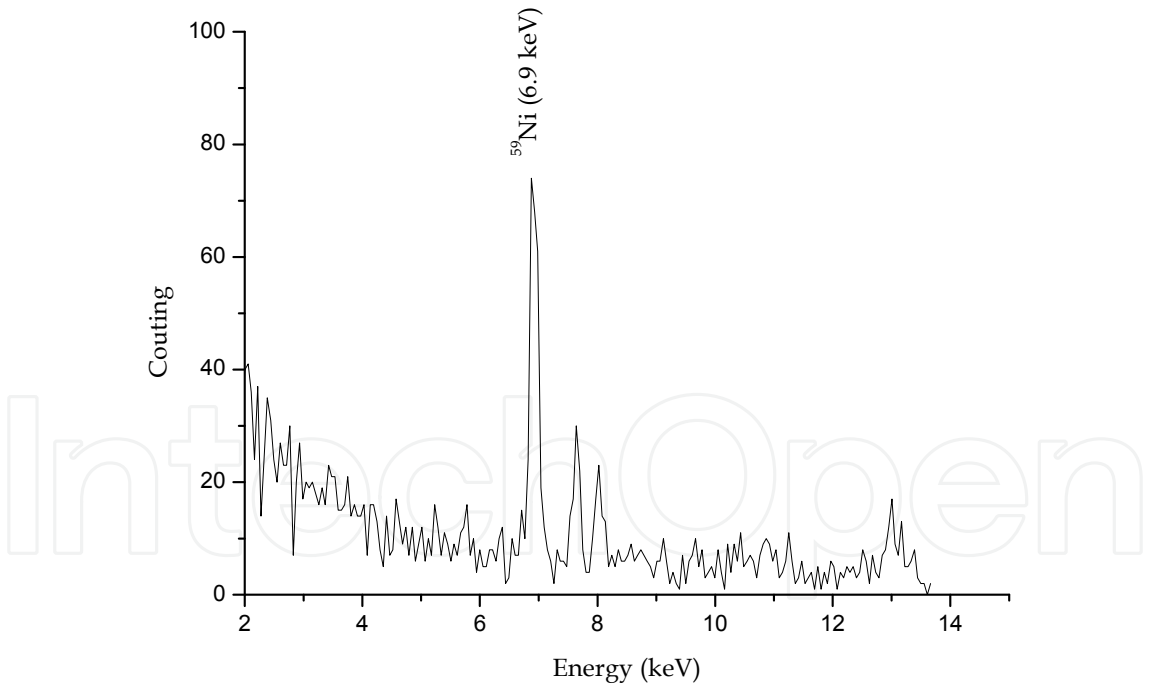


Fig. 3.  $^{59}\text{Ni}$  spectrum for a radioactive waste resin sample

Due to the very long half-life of  $^{59}\text{Ni}$  its radioactivity in radioactive waste samples is normally much lower than  $^{63}\text{Ni}$  (Hou et al., 2005). This was verified by the values obtained for both radioisotopes to the same sample, in the Table 2. According to Scheuerer (Scheuerer et al., 1995) 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 analyzed by

our laboratory the ratio found to vary from 0.03 to 0.14, these values indicate that the concentration activities for  $^{63}\text{Ni}$  are yet bigger than that for  $^{59}\text{Ni}$ . We can, therefore, consider that these ratios are in accordance with that ratio waited for  $^{59}\text{Ni}/^{63}\text{Ni}$ . The Figure 4 shows a typical  $^{63}\text{Ni}$  spectrum of evaporator concentrate sample.

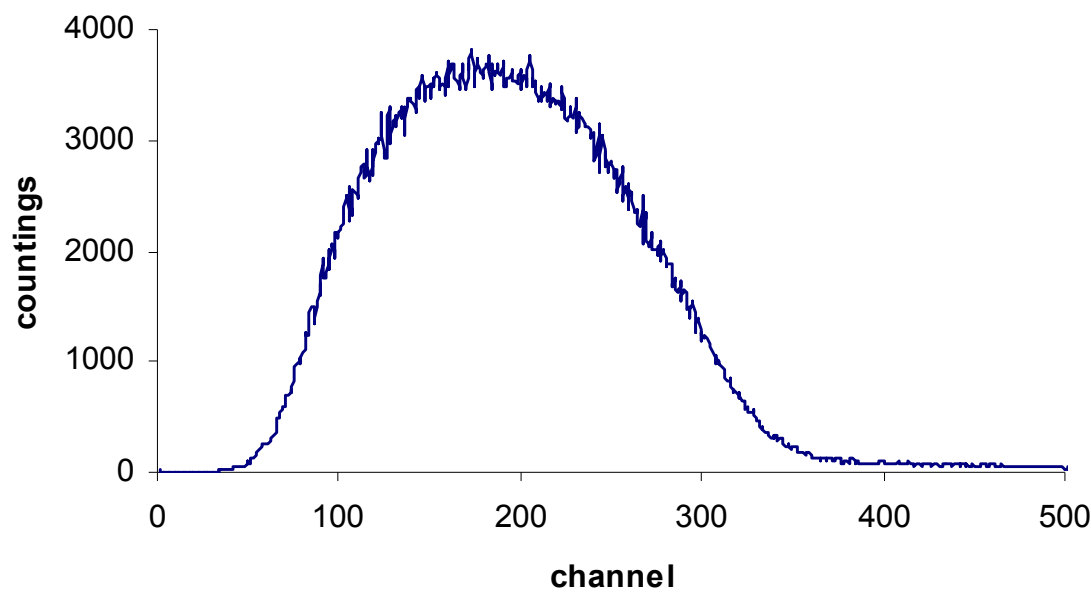


Fig. 4.  $^{63}\text{Ni}$  spectrum for an evaporator concentrate sample

Sample	$^{63}\text{Ni}$ (Bq g <sup>-1</sup> )	$^{59}\text{Ni}$ (Bq g <sup>-1</sup> )
Evaporator concentrate	$31 \pm 2$	$0.86 \pm 0.04$
Ion-exchange Resin	$1.48 \pm 0.07 \times 10^4$	$2.2 \pm 0.1 \times 10^3$
Filter	$5.4 \pm 0.3 \times 10^3$	$2.1 \pm 0.2 \times 10^2$

Table 2.  $^{63}\text{Ni}$  and  $^{59}\text{Ni}$  activities obtained for different types of radioactive waste

4. Conclusions

An analytical procedure for the determination of nickel in nuclear waste samples was developed. The separation of various radionuclides was performed and the use of ammonium hydroxide for separation of nickel from uranium and iron occurred according was proposed. An extraction chromatography was used to purify Ni from the interfering radionuclides. Radionuclides  $^{63}\text{Ni}$  and  $^{59}\text{Ni}$  were determined by LSC and low gamma energy spectrometry after to be purified by Ni resin. It is possible to indicate that when Ni radioisotopes are analyzed by extraction chromatography there are no interferences in the measurement by the techniques utilized.

The chemical yield for Ni was 58% and the detection limit for LSC was 12 Bq/L and the couting efficiency was 75.1%, thus, experiences indicate so far that the method can be used for the analyses of radionuclides in the waste samples.



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. Acknowledgements

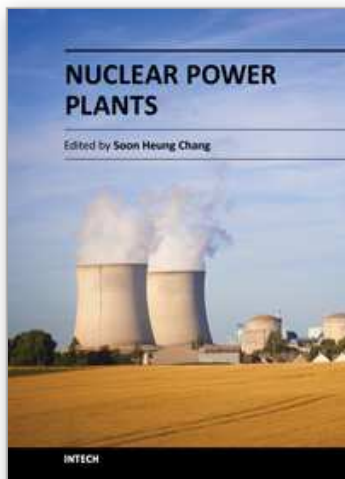
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