



## I-129 DETERMINATION IN EVAPORATOR CONCENTRATE USING OXIDATIVE EXTRACTION AND CHROMATOGRAPHIC RESIN

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### ABSTRACT

Determination of long-lived radionuclides is very important for study of the radioactive waste final deposition. In this work will be studied <sup>129</sup>I radionuclide which present  $1.6 \times 10^7$  years half-life,  $\beta$ -particle-emitting ( $E_{max} = 194 \text{ keV}$ ) and X-ray-emitting ( $E = 29.78 \text{ keV}$ ). It's produced primarily from fission of <sup>235</sup>U and <sup>239</sup>Pu and for fission induced by thermal neutrons. For this reason, radiochemical procedures for <sup>129</sup>I determination in evaporator concentrate wastes from nuclear power plants were carried out. The first procedure was based on oxidative extraction and alkaline absorption and the second one, was based on selective extraction using a chromatographic resin in order to separate iodine from its interferences. After the separation steps, the iodine activity was measured by ultra low gamma spectrometry technique. To set up the yield recovery for <sup>129</sup>I, a tracer solution of <sup>129</sup>I was used in order to follow the behavior of iodine during the separation steps. The yield recovery for iodine was around 75-80% for the first procedure and 80-85% for the second. The two procedures used mutually, ensure a greater efficiency in the separation of iodine from their respective interferences.

**Keywords:** Iodine, Evaporator concentrate, Oxidative extraction, Chromatographic resin

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## 1. INTRODUCTION

The element iodine is a component of thyroid hormone and plays an important role within the human body [1]. According to Chia-Lian [2] the three main sources of radioactive iodine,  $^{129}\text{I}$ , in the environmental are naturally occurring, nuclear weapons testing, and power reaction operation.  $^{129}\text{I}$  has a long half-life ( $t_{1/2}=1.57\times 10^7$  y) which means it will accumulate in biosphere and can enter our body through ingestion or inhalation, and can be absorbed by thyroid [3 - 6]. It is not acceptable  $^{129}\text{I}$  activities in radwastes above the limit of  $0.08 \text{ Ci/m}^3$  near-surface disposal [7].

Due to its long half-life it is one of the most important radionuclides in low and medium radioactive waste from nuclear power plants and it is one of the hard-to-measure radionuclides. The common characteristics of the hard-to-measure radionuclides is that they require radiochemical separations before radiometric analysis [8 - 10].

Measurement of  $^{129}\text{I}$  is not a simple task.  $^{129}\text{I}$  decays by beta particle emission, with maximum energy of 154.4 keV and  $\gamma$ -ray of 39.6 keV, as well as X-rays (24.46, 29.78) keV. It can be measured by  $\gamma$ -ray spectrometry, X-ray spectrometry, liquid scintillation counters (LSC), neutron activation analysis (NAA), accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) [11].

For these reasons was developed in this work a selective radiochemical separation method based on two different methodologies. The first one, based on oxidative extraction and alkaline absorption, and the second one [6], based on chromatographic resin extraction [12].

Once the iodine has been isolated by these methodologies, its activities will be measured by ultra low energy gamma spectrometry technique.

The method was checked in evaporator concentrate samples from Brazilian Nuclear Power Plants – Eletrobrás Termonuclear.

## 2. MATERIALS AND METHODS

All the solution concentrations reported in this paper are expressed as molarity and activity concentrations are expressed as  $\text{Bq.g}^{-1}$  for waste samples.

## 2.1 Reagents and standards

All chemicals were analytical grade.  $^{129}\text{I}$  certified radionuclide solution was obtained from National Institute of Standards e Technology - NIST, SRM 4949C. The Cl resin was provided by TrisKem International and were used as received without further purification.  $\text{Ag}^+$  loaded Cl resin was prepared by contacting 10 g of the Cl resin with 100 mL of a 1 M  $\text{H}_2\text{SO}_4$  solution containing 650 mg of  $\text{AgNO}_3$ .

## 2.2 Samples

The evaporator concentrate samples from different sampling points of nuclear plants were chosen to test the methodology.

## 2.3 Analytical technique

Measurements of  $^{129}\text{I}$  were performed with 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 FWHM, from Camberra (USA).

## 2.4 Separation step

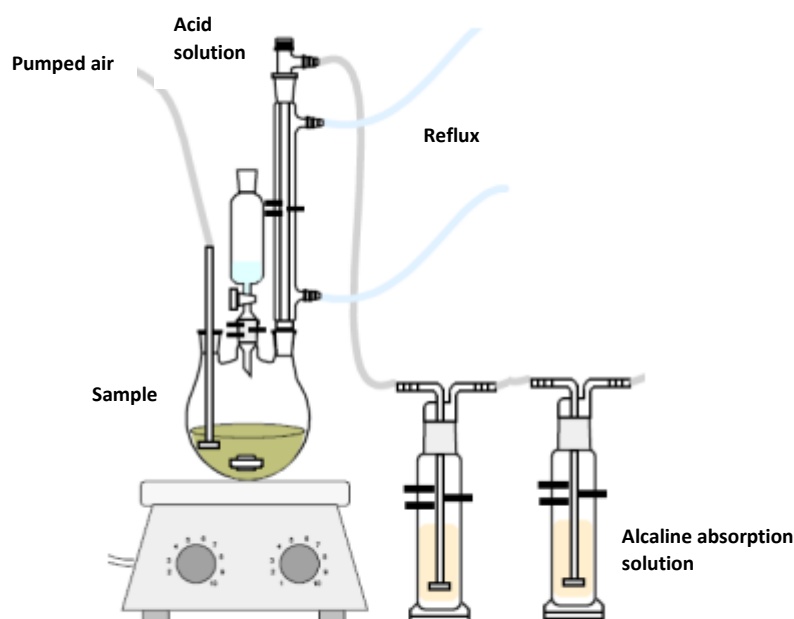
Two radiochemical procedures for  $^{129}\text{I}$  determination were carried out.

### 1 - Oxidative extraction and alkaline absorption

In this procedure, a measured aliquot of sample (~40 mL) is mixed with 1 mL of ammonium iodide ( $\text{NH}_4$ ) and placed under heating in a flask. Then we added 20 mL of concentrated nitric acid ( $\text{HNO}_3$ ) and 4 mL of concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and refluxed for 10 minutes. This procedure is repeated three times. Any inorganic iodine present in the sample is converted to  $\text{I}_2$  form. Air is passed through the reaction flask and the  $\text{I}_2$  is bubbled through 40mL of 3M NaOH solution, where it is absorbed. The separation line for iodine is shown in figure 1. After the absorption step

the alkaline solution is used for  $^{129}\text{I}$ ,  $E_x(\text{keV}) = 30,0$ , determination by ultra low energy gamma spectrometry.

If some spectral interference owing to  $^{137}\text{Cs}$ ,  $E_x(\text{keV}) = 32.19$ , is necessary to carry out a solvent extraction of 3M NaOH solution with toluene at pH near 2 and back extraction with the original alkaline solution.



**Figure 1.** Separation line for iodine

## 2 - Chromatographic resin extraction

In this procedure, a measured aliquot of the sample (~10 mL) was adjusted to 1M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and transferred to the column, which had been prepared with a mixture of 10 ml of  $\text{H}_2\text{SO}_4$  and 650 mg of silver nitrate ( $\text{AgNO}_3$ ). The iodine is retained as silver iodide ( $\text{AgI}$ ) and it is eluted with 10 mL of sodium sulfide ( $\text{Na}_2\text{S}$ ). This elution can be repeated 2 more times. After the separation step the alkaline solution is used for  $^{129}\text{I}$ ,  $E_x(\text{keV}) = 30,0$ , determination by ultra low energy gamma spectrometry. The resins are shown in figure 2.



**Figure 2.** Resins for selective separation of iodine

#### **2.4.1 . Recovery yield step**

For recovery yield determination, a small amount of  $^{129}\text{I}$  was added to the sample as a yield tracer. The  $^{129}\text{I}$  was measured before and after the separation step using Ultra-LEGe detector from CANBERRA.

### **3. RESULTS AND DISCUSSION**

At first, tests were carried out on simulated waste samples containing known amount of  $^{129}\text{I}$  standard solutions in order to check the efficiency and reproducibility of the separations. The protocol was developed on solutions prepared with  $^{129}\text{I}$  standard solution used as a radioactive tracer for the chemical recovery evaluation. The recovery yield obtained was in the range of 75-80% for the first procedure and 80-85% for the second. After, the samples were submitted to separation procedure.

Results obtained with real samples of evaporator concentrate from PWR nuclear-power plants, showed good agreement with the results obtained with the simulated waste samples.

Table 1 shows the results of  $^{129}\text{I}$  determination in evaporator concentrate samples using both procedures.

**Table 1** –  $^{129}\text{I}$  results for concentrate evaporator samples

<b>Characteristics</b>	<b>oxidative extraction/alkaline absorption</b>	<b>chromatographic resin</b>
<b>Sample</b>	$^{129}\text{I}$ specific activity ( $\times 10^{-3}\text{Bq.g}^{-1}$ )	$^{129}\text{I}$ specific activity ( $\times 10^{-3}\text{Bq.g}^{-1}$ )
<b>Evaporator concentrate 1</b>	7.7	8.75
<b>Evaporator concentrate 2</b>	7.3	0.57

The choice of methodology will depend on the type of sample. Chromatographic resins can not be used in samples that require some preparation such as acid attack, evaporation, solubilization and large pH adjustment.

#### 4. CONCLUSION

A radiochemical process was proposed for  $^{129}\text{I}$  determination in evaporator concentrate wastes from nuclear power plants by ultra low gamma spectrometry technique. When working with waste samples from nuclear power plants, chemical separation processes are always needed due its very complex chemical and radiochemical characteristics. Both methodologies presented can be used to  $^{129}\text{I}$  determination.

The main advantages of the proposed procedures are the fast and efficient separation of the iodine, short execution time (~24 h), low consumption of reagents and a good recovery yield.

If any spectral interference occurs after the first procedure, organic solvent extraction will be necessary.

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