

# Determination of Plutonium Isotopes in Radioactive Waste Contaminated with Uranium and Thorium

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**Abstract:** Nucleco is the Sogin Group's Italian leading company in the sector of radiological services, radioactive waste management, decontamination and reclamation of industrial sites and nuclear power plants. Nucleco is 60% owned by Sogin and 40% by ENEA— National Agency for New Technologies. The waste characterization carried out by Nucleco SpA includes a large variety of radionuclides belonging to the gamma, beta and alpha emitter families. The determination of Uranium and Plutonium isotopes plays a key role in the waste characterization. Nucleco SpA has distinguished itself in characterizations of radioactive waste in complex and nuclear plant matrices. These matrices have large amounts of alpha emitters, in particular isotopes of Uranium, Thorium and Plutonium. A significant presence of U238 results in such a large amount of Th234 (and daughters) that interferes with the determination of Pu241. Hence, there is the need of finding a pre-treatment, extraction and subsequent purification technique that would allow Th234 to be detached and thus Pu241 to be determined in complex high-activity matrices. The above elements are extracted using chromatography columns. An isotope of the element to be analyzed, with known activity, is added at the beginning of the process to determine the extraction yield. Before being eluted into the column, the sample undergoes a series of treatments in order to be purified of any interferents. The method developed by Nucleco involves the oxidation of Pu at valence +6 and the subsequent precipitation, in fluorides form, of the elements with valence +4 and +3 (i.e. Th234). Pu241 is then measured by LSC (Liquid Scintillation Counting), while the other isotopes are measured by alpha spectrometry after electrodeposition on a metal plate.

Key words: Plutonium, thorium, purification, liquid scintillation, LSC, alpha emitters, beta emitters.

# 1. Introduction

The safety and management of radioactive waste mainly uses radiological characterization by destructive and non-destructive analysis to obtain the most detailed qualitative and quantitative radiological information possible. As far as non-destructive analysis, gamma detectors are used and different methods can be applied to measure and analyze the radiological content [1].

Regarding destructive analysis, samples are brought to a liquid state, if they are not yet, and chromatographic extractions are made on this solution. These operations take place using an ion-exchange resin that takes advantage of the different oxidation state and affinity of the elements with the stationary phase of the column to achieve separation.

# 2. Start-Up Phase

Before beginning a plutonium extraction, it is necessary to trace the sample with a known amount (1 Bq) of an isotope different from the one to be analyzed, in order to determine the extraction yield. For example, to determine the presence of Pu238, Pu239, Pu240, and Pu241 [2], usually Pu242 is used as a tracer.

## **3.** The Extraction

After tracing,  $Ca(NO_3)_2$  and a saturated solution of oxalic acid is added to the solution. After this, the solution is brought to pH 4 by the addition of NH<sub>4</sub>OH [3].

The pH 4 will create conditions for calcium oxalates to form, which, in turn, act as adjuvants for the precipitation of Plutonium in the form of oxalate (Fig. 1).

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Fig. 1 Oxalate solution, after centrifugation.

This first step is common to all alpha radionuclide extractions used by Nucleco, as it serves to remove many interferents, such as metals and organic compounds. After that, however, it proceeds differently for each radionuclide; we will illustrate the case of Plutonium. The solid phase is dissolved in HNO<sub>3</sub> and fixed on a hot plate, and heat treated with repeated additions of  $H_2O_2$  until the complete dissolution of the oxalates. Subsequently, the solution is brought up to HNO<sub>3</sub> 8 M.

 $FeCl_3$  is then added, which will make the solution yellow due to  $Fe^{3+}$  in solution that will act as an indicator of the oxidation state.

By adding NaNO<sub>2</sub> the solution will turn from yellow to dark green, in fact the iron will be reduced from  $Fe^{3+}$ to  $Fe^{2+}$ , along with Pu which will have valence +3 and +4 (Fig. 2).

The solution obtained is poured into a chromatographic column packed with ion exchange resin. The ion exchange resin is conditioned with HNO<sub>3</sub> 8 M.

The HNO<sub>3</sub> environment allows the creation of bonds with the Pu which are retained by the column, while the americium and curium are eluted together with the Fe, Calcium and other interferents.

Pu is released from the column by means of an HClhydroxylamine solution, or HCl-HI solution, and it is recovered into a beaker (Fig. 3).

The hydroxylamine (or HI) will react with Pu, retained in the column, by changing the oxidation state of Pu allowing it to elute.



Fig. 2 Reduction from  $Fe^{3+}$  to  $Fe^{2+}$ , which acts as an indicator by changing from yellow-brown to dark green.



Fig. 3 A chromatographic column and back beakers with evaporating solutions.

An aliquot intended for LSC spectrometry for the determination of Pu241[4] is subtracted from the sample. The other solution is electrodeposited on INOX plate by an electrodepositor with a  $\Delta$ = -1.20 V or larger (Fig. 4). The INOX plate is counted in an alpha spectrometer (Fig. 5) [5].



Fig. 4 Electrodepositor.

#### 3.1 Purification of Pu241 from Th234

Generally, Th234, together with other interferers, is eliminated during extraction in the column packed with Dowex resin.

If the sample is very rich in Th234 this may not be enough, and we must proceed with the elimination by precipitation.

The presence of Th234 in the spectrum makes impossible to calculate the activity of Pu241 and the activity in "total alpha" (Pu242 + Pu239 + Pu240 + Pu238 required to determinate the recovery yield). The result is simulated in Fig. 6.

To remedy this, it is therefore necessary to selectively eliminate Th. At Nucleco laboratories, a method is used to precipitate them as fluorides and eliminate them by centrifugation.



Fig. 5 Alpha spectrometer.

After eluting from the column as described above, the Pu is oxidized to +6 by bringing the sample into an oxidizing environment, usually in concentrated HNO<sub>3</sub> and  $H_2O_2$ .

Cerium or Lanthanum is added to the resulting solution, which will act as an adjuvant for the precipitation of ThF<sub>4</sub>.

By adding a saturated solution of NaF drop by drop, fluorine will react with cerium (or lanthanum) [6], causing the +4 and +3 valence interferents to precipitate, leaving Pu in solution, which has previously assumed a +6 oxidative form, unrelated to forming bonds with fluorine.

The solution is centrifuged and the supernatant containing Pu is recovered while, the precipitate containing Th, is discarded.

The supernatant is then brought to a condition to be measured in LSC.



Fig.6 In the image, a beta spectrum of Pu241 contamination can be seen in red where, both the element and total alpha region can be identified, while superimposed in blue one can see the beta emission of Th234 which makes the spectrum impossible to analyze.

In the sample under analysis, all Pu<sup>6+</sup> will be found that has not reacted with NaF, while the interference caused by the presence of Th will have disappeared, making the activity of Pu241 in LSC vial appreciable.

### 4. Calculation of the Activity and Conclusion

To obtain the activity concentrations it is necessary to evaluate: the quantity of sample being analyzed, the process yield and the efficiency of the detector [7].

Hence:

$$A = \frac{CPM}{60 * eff * M * y}$$

where:

A = Activity concentration of the nuclide (Bq/g)

*eff* = Efficiency

$$M =$$
 Mass of the sample sent to measure (g)

y = Recovery yield of the process

*CPM* = Counts per minute of sample And [8]:

$$MDC = \frac{2.71 + 3.29 * \sqrt{CPM_b * t_c * \left(1 + \frac{t_c}{t_b}\right)}}{60 * eff * M * y}$$

where:

 $t_b$  = White counting time (min),

 $t_c$  = Sample counting time (min),

 $CPM_b$  = Counts per minute of blank.

While the recovery efficiencies of alpha emitters are evaluated using tracers of  $\alpha$ -emitters (Pu242), which obviously emit at different energies from those analyzed, an example of which is:

RR = Final tracer activity/Tracer activity used

The recovery yield of Pu241 is the one that requires a slightly different processing, as it is calculated with the support of the alpha spectrometry count. It is in fact necessary to first evaluate the percentage of counts due to the tracer in alpha spectrometry, and then multiply it by the integral of the alpha counts, obtained from liquid scintillation. The counting efficiency will therefore be the ratio between the value just calculated and the tracer inserted.

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