The Development of a rapid method for Plutonium separation by extraction chromatography and its application for environmental samples

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Abstract. This research aims to develop a rapid method of plutonium analysis from sediment samples using the extraction chromatography method with TRU resin. This approach will be compared with the anion exchange method with DOWEX resin previously conducted in the BATAN radioecology laboratory. Plutonium measurements was carried out using an alpha spectrometer with a PIPS detector after the separation processes. The results showed that recovery using extraction chromatography followed by the microprecipitation method resulted in an average recovery of 71.22 percent, compared to anion exchange using the electrodeposition method, which obtained about 58.89 percent. Since a combination of chromatographic extraction with electro-deposition, the recovery is still low, about 27.56 percent. The chromatographic extraction method with microprecipitation method to sediment samples from the coast of Merak resulted in an average activity of 0.14 Bq/kg dry. The activities obtained are comparable with the previous data from the Merak coastal sediment study. The advantages of using the extraction chromatography method compared to using the anion exchange method to separate plutonium from sediment samples are the shorter separation time and the less acid waste produced. Another advantage is that it is more selective to separate plutonium from other actinides. This approach is very suitable for emergency preparedness when there is an emergency response.

Keywords: Plutonium-239/240, extraction chromatography, ion exchange, sediment sample

1. Introduction
Artificial radionuclides have been widespread in recent times, with ecological consequences for the environment. In the radioecological aspect, increase the background radiation will has an impact on the quality of the environment. One of the artificial radionuclides that have an environmental impact is plutonium-239/240. Plutonium-239/240 is released into the environment as a result of human activities using nuclear materials such as nuclear weapons testing, routine discharge or nuclear accident releases from nuclear power plants, and nuclear fuel reprocessing [1]. The Fukushima Dai-ichi nuclear accident releases radionuclides directly into the Pacific Ocean, such as cesium-137 and plutonium-239/240 and other anthropogenic radionuclides, which have caused serious contamination of the marine environment [2].
The Pacific Ocean, located in the northern latitudes, receives quite a large number of fallout radionuclides. Radionuclides that released into marine waters, due to marine waters' chemical and physical properties, will follow the currents, and some of them will settle and eventually deposited in sediments. The movement of seawater from the Pacific Ocean to the Indian Ocean will enter Indonesian marine waters through known as Indonesian Through Flow (ITF) [3] and is one of Indonesia's focuses on studying anthropogenic radionuclides in Indonesian marine waters like plutonium.

Plutonium research has been carried out in Indonesia, such as in Jakarta Bay [4] the coast of Bangka Island [5] Karimata Strait [3] and in Gresik Coastal waters [6]. The analysis of plutonium-239/240 that carried out so far uses the ion exchange method with DOWEX resin as a separation method. Plutonium analysis using this method is very complicated and time-consuming and requires a large amount of acid solution, and is not suitable for emergency response.

Many methods have been developed to analyse radionuclides in environmental samples, such as the chromatographic extraction method used by TRU resin to separate plutonium from environmental samples [7–12], which has never been done in Indonesia before. This method uses the deposition method with iron (III), separation using the extraction chromatography method with TRU resin in neodymium fluoride.

Two method uses in conjunction from the separation method to the nuclide to be measure are electrodeposition and microprecipitation methods. Electrodeposition is a coating process of thin layer of metal on the top of different metal using the electrical [13]. In this case, plutonium will coat onto the stainless steel plate. Microprecipitation, making it a preferred method compared to electrodeposition, has a high yields and good peak resolutions and the process is faster yet more efficient compared to electrodeposition[14].

To prepare a fast and less acid method that is suitable for emergency response, a separation method by extraction chromatographic for plutonium analysis carried out using the IAEA reference material. That method will compare with the ion exchange method using DOWEX Resin. The commercially Eichrom extraction chromatographic resins (TRU Resin) was chosen as a potential resin for the separation and purification procedures. The chosen method will apply to analyse sediment samples from the coastal areas of Merak. Then the new method will applied to replace the previous method as a rapid response to nuclear emergencies.

2. Method

2.1. Sample pre-treatment and digestion

10 g sediment and soil Reference Material IAEA-375 were dry ash at 550°C for 6 hours. The ash sample with 239Pu tracer digested with hydrogen peroxide and concentrated nitric acid. The final digested samples dissolved in 8 M nitric acid and 10 g sodium nitric, boiled for 30 minutes. Before heated near to dryness, the sample was filtered through glass-fiber filter papers [13].

2.2. Dowex Resin separation for plutonium

The column filled with 10-ml Dowex resin and flow water, and 8 M nitric acid. Samples (from 2.1. Section) diluted in 8 M nitric acid and fed to the column of ion exchange at a flow rate of 1 ml/ min. The column was washed with 8 M nitric acid, and then with 7.8 M hydrochloric acid. Plutonium eluted with 1 M ammonium iodide - 9 M hydrochloric acid. The eluent was evaporated until dryness [13,14].

2.3. TRU resin separation for plutonium

Samples (from 2.1. Section) diluted in 1 M hydrochloric acid and Ca containing solution, Mohr salt, and hydrazine added to the solution. Each sample has adjusted the pH to 3- 4 and warm. Hydrofluoric acid added before centrifuged the solution. The precipitate collected, and a hot 2 M nitric acid added
before transferred to a 100ml glass beaker. Each sample solution added with 400 mg boric acid and warmed to help dissolution before adjusted to the desired oxidation states of plutonium by adding sodium nitric. The plastic chromatographic column filled with the soaked TRU resin then washed with distilled water, 2 M nitric acid, and 0.01 M sodium nitric solution. The sample solution passed through to the TRU resin column. Wash the column with 4 M hydrochloric acid to remove americium. Plutonium was eluted with 4 M hydrochloric acid - 0.01 M titanium (III) chloride [15,16].

2.4. Electrodeposition Processing
Eluent (from 2.2. Section) was evaporated until dryness, nitric acid and peroxyde were added and evaporated to dryness again. Each sample was diluted with sulfuric acid 5% and was set a pH of about 2 [13]. Samples electroplated onto stainless steel disks. The electrodeposition was performed using an electrolysis apparatus with an electrodeposition cell consisting of a Teflon cylinder, an anode of stainless steel disk and a cathode of the platinum electrode, and [9].

2.5. Microprecipitation Processing
The eluent (from 2.3. Section) was added with 100 μl 15 % titanium (III) chloride, followed with 10 mL distilled water, 100 μl of the stock solution containing 50 μg Nd/100 μl, and 5 ml 40 % hydrofluoric acid. The sample was let it stand for half an hour after shaking. The sample solution filtered through membrane that has a 0.10 μm pore size. The membrane filter has to be wetted with alcohol before passing the aqueous solution. The beaker rinsed with 4% hydrofluoric acid and, ethanol. Finally, the funnel rinsed with ethanol too. The membrane filter is dried at ≤ 50°C, then mounted on a metal sample holder and counted in the alpha spectrometer [15].

2.6. Alpha spectrometer counting
Plutonium measured by alpha analyst Canberra's 7200-02 model equipped with Apex Alpha™ software. This equipment has eight PIPS (Passivated Implanted Planar Silicon) detectors for measuring eight samples simultaneously.

2.7 Calculation of Plutonium Activity
To calculate the activity of $^{239, 240}$Pu, the following equation has been used [19]

$$A_A = \frac{A_A}{m_{a-q}} \cdot f_1 \cdot f_2 \cdot f_3 \cdot f_4 \quad \text{in Bq/kg}$$

(1)

At the date of sample collected, with:

$$A_A = C_T \cdot V_T \cdot \left[ \frac{R_{GA} - R_{BA}}{R_{GTA} - R_{BTA}} - q_I \right] \cdot \left( \frac{P_{aT}}{P_{aA}} \right) \quad \text{in Bq}$$

(2)

Where $m_a$ is mass of sample (gram), $q$ is sample wet/dry ratio, $f_1, f_2, f_3$ and $f_4$ are the correction factor. $C_T$ and $V_T$ are tracer activity and volume, $R_{GA}$ and $R_{GT}$ are gross counting of sample and tracer, $R_{BA}$ and $R_{BT}$ are blank counting rate of sample and tracer, $q$ is isotopic impurities of the tracer and $P_{aT}$ and $P_{aA}$ are sum of alpha emission peak of tracer and sample.

3. Result
3.1. The adjustment of valence in digestion processes.
Adjustment of valence is an important step in the separation of plutonium because, in the environment, plutonium is usually in the complex Pu (III), Pu (IV), and Pu (V). The converted redox reagents used to convert such as sodium nitric, peroxyde, sodium sulfide, and potassium meta-bisulfite. If used an anion-exchange resin or an extraction resin for plutonium separation, plutonium's valence state usually converted to Pu (IV). In this study, sodium nitric solution is used to convert all valence plutonium to Pu (IV) [7,16].

Sodium nitric solution convert all valence plutonium before sample solution flow to the resin. Then, the resin bed washed with nitric acid before Americium desorption with hydrochloric acid. This
step was useful to eliminate interferences of americium and other radionuclides. Titanium (III) chloride in 4 M hydrochloric acid used to extract plutonium from the resin. Separation of plutonium from americium is an important step for alpha spectrometry to eliminate potential interferences. In alpha spectrometry, peak energy of $^{241}\text{Am}$ and $^{238}\text{Pu}$ was overlap (5.48 and 5.50 MeV) [7,12].

### 3.2. Ion Exchange Method using Dowex Resin

The ion exchange method tested to analyze certified reference materials IAEA (Reference Material IAEA-375) from the International Atomic Energy Agency. The dry sample processed based on the above procedure, and the plutonium isotopes measured with alpha spectrometry. The recovery results for IAEA-375 shown in Table 1 below.

**Table 1. $^{239/240}\text{Pu}$ result for anion exchange method with electrodeposition.**

| No | Sample code | $^{239/240}\text{Pu}$ Recovery (%) | $^{239/240}\text{Pu}$ Reference Value Bq/kg | $^{239/240}\text{Pu}$ Measured Value Bq/kg | Difference (Bq/kg) |
|----|-------------|-------------------------------------|---------------------------------------------|------------------------------------------|-------------------|
| 1  | Dowex – C1  | 88.30                               | 0.300                                       | 0.265                                    | 0.035             |
| 2  | Dowex – C2  | 42.26                               | 0.300                                       | 0.127                                    | 0.173             |
| 3  | Dowex – C3  | 45.92                               | 0.300                                       | 0.138                                    | 0.162             |

In the separation process, using the ion exchange method, it found that the separation process carried out was longer than the extraction chromatography method. The leaching and pre-treatment process requires much nitric acid and hydrochloric acid and a large volume of acid waste, as much as 400 ml for each sample. The separation process also took a total time of about 9 hours.

The recovery of plutonium isotopes was obtained by measuring the chemical yield of $^{239/240}\text{Pu}$ from each sample. Recoveries of plutonium isotopes for the different samples shown in Table 1. The average of plutonium recovery in all samples was low (58.88%). However, one sample showed high recovery (Dowex – C1: 88.33%).

### 3.3. Extraction Chromatography Method using TRU Resin

The extraction chromatography method is faster than the ion exchange method and acid solution used for pre-treatment is not too much. The column used in this method is small, with a smaller resin amount, but resin price is costly. The time required for the separation process is faster, which is about 1 hour. The total acid waste is 50 ml. The plutonium analysis of three references material from the IAEA using the extraction chromatography method shown in Table 2.

**Table 2. $^{239/240}\text{Pu}$ result for extraction chromatography method with electrodeposition and microprecipitation.**

| No  | Sample Code | $^{239/240}\text{Pu}$ Recovery (%) | $^{239/240}\text{Pu}$ Reference Value Bq/kg | $^{239/240}\text{Pu}$ Measured Value Bq/kg | Difference (Bq/kg) |
|-----|-------------|-------------------------------------|---------------------------------------------|------------------------------------------|-------------------|
| **Electrodeposition Method** |
| 1   | TRU-C1 A    | 44.40                               | 0.300                                       | 0.113                                    | 0.187             |
| 2   | TRU-C2 A    | 21.30                               | 0.300                                       | 0.063                                    | 0.237             |
| 3   | TRU-C3 A    | 24.23                               | 0.300                                       | 0.072                                    | 0.228             |
| **Microprecipitation Method** |
| 1   | TRU-C1 B    | 76.67                               | 0.300                                       | 0.230                                    | 0.070             |
| 2   | TRU-C2 B    | 66.00                               | 0.300                                       | 0.198                                    | 0.102             |
| 3   | TRU-C3 B    | 71.00                               | 0.300                                       | 0.213                                    | 0.087             |
In Table 3, the average recovery of plutonium using the electrodeposition method is very small, which is 27.56%. Meanwhile, the average recovery of plutonium using the microprecipitation method was relatively high, 71.22%.

The $^{239/240}$Pu separation process is similar to previous studies because it is a selective and fast separation method for separating radionuclides in environmental samples. This extraction chromatography method produces less acid waste solution than the ion exchange method. This method's weakness is the expensive resin compared to the exchange resin method [17].

Many laboratories use chromatographic extraction resins such as TRU to separate plutonium in water, soil, and sediment samples. TRU resin is used in the comparison test (PROCORAD) with good results and used as a routine procedure in several laboratories [18].

### 3.4. Analytical applications for environmental samples

The TRU extraction chromatographic separation followed by the microprecipitation method takes about one hour per sample, and the full analysis process can be done in eight hours. Compared with the ion exchange methods, the separation efficiency much improved, so that the proposed method was therefore suited for the rapid and convenient determination of plutonium in environmental risk assessment and radiological emergencies.

The proposed method was chosen for plutonium analysis on sediment samples from the coastal area of Merak Beach. The analysis results obtained $^{239/240}$Pu activity with an average of 0.14 Bq/kg. The activities obtained were compared with the previous Merak coastal sediment analysis data.

| No | Sample Name | Activity plutonium (Bq/kg) |
|----|-------------|--------------------------|
| 1  | Merak 1     | 0.115                    |
| 2  | Merak 2     | 0.165                    |

### 4. Summary

The results showed that recovery using extraction chromatography followed by the microprecipitation method resulted in an average recovery of 71.22 percent, compared to anion exchange using the electrodeposition method, which obtained about 58.89 percent. Although using a combination of chromatographic extraction with electrodeposition, the recovery is still low, around 27.56 percent. The advantages of using the extraction chromatography method to separate plutonium from sediment samples are the shorter separation time and less acid waste than using the anion exchange method. Another advantage is that it is more selective to separate plutonium from other actinides. The chromatographic extraction method applied to sediment samples from Merak Coastal resulted in an average activity of 0.14 Bq/kg dry. The activities obtained were comparable with the previous Merak coastal sediment analysis data. Because the time used is shorter and results in less acid waste, this method is very suitable for emergency preparedness when an emergency response occurs.

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