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To cite this article: S Nuchdang et al 2018 J. Phys.: Conf. Ser. 1144 012071

View the article online for updates and enhancements.
Studies on the possibility of determination of uranium and thorium concentration in the Thai monazite ore processing samples using gamma-ray spectrometry technique

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Abstract. The possibility of the determination of U and Th concentration in the Thai monazite ore processing samples using gamma-ray spectrometry technique was investigated. The studied samples were monazite ore, tri-sodium phosphate, mixed rare earth hydroxide, enriched cerium, uranium cake, thorium cake, La₂O₃ and CeO₂. The measured activity concentrations of ²³⁸U and ²³²Th were converted into the concentrations of U and Th under the assumption of secular equilibrium. The results showed that the major daughter nuclides found in the studied samples, were ²¹⁴Pb, ²¹⁴Bi and ²₂₆Ra for ²³⁸U series with additional radionuclides of ²²⁸Ac, ²¹²Pb, ²⁰⁸Tl and ²¹²Bi for ²³²Th series. The concentrations of U and Th estimated via each daughter products of their series were not significantly different for all samples. Wavelength Dispersive X-ray Fluorescence (WDXRF) with different sample preparations (loose powder, pressed pellet and fused bead methods) was also used to determine the concentrations of both U and Th in these samples. A good agreement between the concentration of U and Th measured by gamma-ray spectrometry (U = 0.42 wt%, Th = 6.54) and WDXRF prepared by fused bead method (U = 0.41 wt%, Th = 7.37) was observed for monazite ore sample.

1. Introduction

There are different destructive and non-destructive methods used for the determination of uranium (U) and thorium (Th) in ore, soil, sand and rock samples. Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are destructive methods while neutron activation analysis (NAA), X-ray fluorescence (XRF) and gamma-ray spectrometry are non-destructive methods capable for U and Th analysis [1,2,3]. For ICP-MS and ICP-OES methods, the concentrations of U and Th can be directly measured with excellent results in terms of sensitivity, precision and accuracy, however they need the sample pre-treatment step. In addition, the limitations of both techniques are the occurrences of spectroscopic (spectral interference) and non-spectroscopic (matrix effect) interferences [4,5].
Even though NAA as a potential non-destructive method can precisely measure the total U and Th in the samples, it has some drawbacks like a lack of appropriate neutron sources, either a nuclear research reactor or a neutron generator [5]. XRF method offers numerous advantages including: relatively simple sample preparation, non-destructive method as well as simultaneous multi-element qualitative and quantitative analysis [5]. Nevertheless, typical detection limits for XRF are in the ppm range, which is not satisfactory for several applications [6]. Gamma-ray spectrometry is a valuable tool for determining and characterizing radioactive content in various samples; the irradiated materials, soils, rocks, mineral deposits, and environmental. This efficient methods is utilized to measure the natural radioactivity (235U, 232Th decay series and 40K) in monazite rich black sand beach of Penang Island, Malaysia [7] and monazite-rich sands in the State of Espirito Santo, South Eastern Brazil [2].

Thai monazite ore composes of rare earth elements (La, Ce, Pr, Nd, Y, Sm, Gd and Dy) in the range of 50-60%, uranium of 0.5% and thorium of 8%. The break-down of monazite ore at Thailand Institute of Nuclear technology was carried out using alkaline method. The monazite ore was ground and digested with NaOH at high temperature (≥120 °C). This step produced the mixed rare earth hydroxide and by product, tri-sodiumphosphate. The mixed rare earth hydroxide was dissolved in HCl and Th and U was precipitated out by NaOH. After the precipitation, the uranium and thorium cakes were separated by solvent extraction process. The enriched cerium was obtained by the precipitation of the mixed rare earth chloride using NaOH. The ion exchange process was used to separate pure cerium oxide and pure lanthanum oxide from the enriched cerium.

In this work, gamma-ray spectrometry was developed as an alternative method of the determination of U and Th concentrations in the monazite ore processing samples as carried out at Thailand Institute of Nuclear technology. The evaluation and comparison with the WDXRF method was also carried out.

2. Materials and methods

2.1. Sample preparation

Samples used in this study were the Thai monazite ore, tri-sodiumphosphate, mixed rare earth hydroxide, enriched cerium hydroxide, uranium cake, thorium cake, pure cerium oxide and pure lanthanum oxide. These samples were obtained from the Thai monazite ore processing at Thailand Institute of Nuclear Technology. All samples were dried at 110 °C to remove the moisture from the samples. The dried samples were ground and passed through 45 mesh sieve.

The sieved samples were weighed and then transferred into a 1000 ml Marinelli beaker (Marinelli beaker sample preparation method) or a small cylindrical polyethylene container (point source sample preparation method). These samples were carefully sealed and stored for more than 30 days to achieve secular equilibrium between thorium and radium and their progenies.

2.2. Gamma-ray spectrometry analysis

Gamma-ray spectrometry measurement was performed using a p-type HPGe coaxial detector with 57 mm diameter and 56 mm thick crystals. Full width of half maximum (FWHM) of the spectrometry system was 1.85 keV at 1332 keV of Cobalt-60 gamma-ray line. The detector was coupled with multichannel analyzers for data acquisition. Quantum Gold from Princeton Gamma Tech was used to analyze the spectra. The samples were counted for 8000 seconds.

2.2.1. Energy calibration. Energy calibration of the HPGe detector was carried out before the analysis using the standard radioactive sources of 133Ba (53.30, 81.09, 276.80, 303.20, 356.40, 384.30 keV), 137Cs (662.20 keV), 109Cd (1174.00, 1333.40 keV), 57Co (122.1 keV), 22Na (1275.40 keV).

2.2.2. Efficiency calibration. Efficiency calibration of the HPGe detector was performed using the standard radioactive sources of 241Am (59.54 keV), 109Cd (88.03 keV), 57Co (122.10 keV), 137Cs (661.66 keV), 60Co (1172.37, 1332.50 keV) for Marinelli beaker analysis, and 133Ba (53.13, 81.00,
276.80, 302.85, 356.01, 383.85 keV), $^{137}$Cs (661.66 keV), $^{60}$Co (1172.37, 1332.50 keV), $^{57}$Co (122.06 keV), $^{22}$Na (1275.40 keV) for point source analysis. A fourth order polynomial equation with the best fit for Marinelli beaker and point source methods were obtained.

2.2.3. Activity concentration calculation. The activity concentrations of $^{238}$U and $^{232}$Th can be computed using the gamma ray photopeaks of their daughter products. A list of efficiency values and the gamma-ray energy of the decay daughters of $^{238}$U and $^{232}$Th used to determine the activity concentrations are given in Table 1. The formula applied to compute the activity concentration of $^{238}$U and $^{232}$Th is as follows:

$$A = \frac{C_n \times 1000}{\varepsilon \gamma \times P \gamma \times m} \quad (1)$$

where $A$ is the activity concentration in Bq kg$^{-1}$, $C_n$ is the net count per second of the resulting photo peak, $\varepsilon_{\gamma}$ is the efficiency of the HPGe detector at the corresponding gamma-ray energy, $P_{\gamma}$ is the emission probability per decay corresponding to the gamma-ray energy and $m$ is the mass of the sample in kg.

Table 1. Efficiency values, emission probabilities and gamma energies of the decay daughters of $^{238}$U and $^{232}$Th used to determine the activity concentrations for Marinelli beaker and point source methods.

| Parent radionuclide | Daughter radionuclide | Energy (keV) | Emission probability (%) | Efficiency |
|---------------------|-----------------------|-------------|--------------------------|------------|
| U                   | $^{226}$Ra            | 186.21 (13) | 3.56 (19)                | 0.0250     | 0.0092     |
|                     | $^{214}$Pb            | 295.22 (2)  | 18.41 (36)               | -          | 0.0064     |
|                     |                       | 351.93 (2)  | 35.60 (7)                | 0.0180     | 0.0056     |
|                     | $^{214}$Bi            | 609.31 (7)  | 45.49 (19)               | -          | 0.0036     |
| Th                  | $^{228}$Ac            | 338.32 (6)  | 11.72 (41)               | -          | 0.0058     |
|                     |                       | 911.21 (6)  | 26.5 (8)                 | 0.0080     | 0.0026     |
|                     |                       | 968.97 (5)  | 16.1 (5)                 | 0.0024     |
|                     | $^{212}$Pb            | 338.63 (2)  | 43.6 (5)                 | 0.0235     | 0.0078     |
|                     |                       | 300.09 (12) | 3.18 (14)                | -          | 0.0063     |
|                     | $^{212}$Bi            | 727.33 (9)  | 6.65 (4)                 | 0.0098     | 0.0031     |
|                     | $^{208}$Tl            | 510.74 (2)  | 22.5 (2)                 | 0.0115     | 0.0041     |
|                     |                       | 583.19 (2)  | 85.0 (3)                 | -          | 0.0038     |

2.2.4. U and Th concentrations calculation. The activity concentrations of $^{238}$U and $^{232}$Th were converted into the concentrations of U and Th, respectively according to the following relationship [8]:

$$1 \text{ mg kg}^{-1} \text{eU} = 12.35 \text{ Bq kg}^{-1} \text{ of U}^{238} \quad (2)$$
\[ 1 \text{ mg kg}^{-1} \text{eU} = 4.06 \text{ Bq kg}^{-1} \text{ of Th}^{232} \] (3)

2.3. **Wavelength dispersive X-ray fluorescence (WDXRF) analysis**

The concentrations of U and Th were also measured by WDXRF technique. The sample preparations were done using the methods described by Lertsathitphong et. al. [9]. The sample preparation methods including the loose powder, the pressed pellet powder with the amount of sample of 40 wt%, and the fused bead with the amount of sample of 12 wt% were investigated.

3. **Results and discussion**

Table 2 and 3 shows the concentrations of U and Th in wt% or mg kg-1 units measured by the gamma-ray spectrometry as calculated via their decay daughter products for the monazite processing samples. It can be noted that the major radionuclide, 228Ra, 214Pb and 214Bi for the 238U decay series as well as 226Ac, 212Pb, 208Tl and 212Bi for the 232Th decay series in the monazite processing samples could be detected by the gamma-ray spectrometry technique. The concentration values of U and Th calculated via their own daughter products were not significantly different. It means that the U and Th decay chains were in secular equilibrium. The standard deviation and coefficient of variation of U and Th measurements were less than 5% and 10%, respectively for all samples except for the Th measurement of tri-sodium phosphate sample.

The concentrations of U and Th in the monazite ore processing were also determined by the WDXRF with different sample preparations such as the loose powder (LP), the pressed pellet (PP) and the fused bead (FB) methods. As can be seen in Table 2 and 3, the mean concentration of U in monazite ore sample measured by the gamma-ray spectrometry of 0.42 wt% was found which was good agreement with that obtained by the WDXRF prepared by the PP and FB methods (0.41 wt%).

For Th, a fairly well agreement between the result values obtained by the gamma-ray spectrometry (6.54 wt%) and the WDXRF prepared by FB method (7.37 wt%) was observed.

In case of the mixed rare earth hydroxide sample, the concentration of U ranging from 0.38-0.42 wt% was detected by the WDXRF, however for the gamma-ray spectrometry with Marinelli beaker method, the concentration of U could not be determined. It is because of the high density matrix of the sample leading to the reducing of the counting efficiency. No photo peaks indicated to U, were found when the point source geometry was employed. The mean concentration of Th in this sample measured by the gamma-ray spectrometry was found to be 5.84 wt%. This result value and the value determined by WDXRF, differed by more than 30%.

For tri-sodium phosphate sample, the concentrations of U and Th for the gamma-ray spectrometry measurements were 132.44 and 0.88 mg kg\(^{-1}\), respectively. The WDXRF measurement using the LP and PP method could detect the concentration of U, however those values did not relate to the values obtained by the gamma-ray spectrometry. There was no Th, was observed in this sample by the WDXRF technique. Interestingly, the gamma-ray spectrometry can be efficiently determined the concentration of U (22.69 mg kg\(^{-1}\)) and Th 38.90 (mg kg\(^{-1}\)) in the enriched cerium samples whereas the WDXRF was no sensitive to detect those values.

There was obvious difference between the result values obtained by the gamma-ray spectrometry and the WDXRF for U and Th measurements in the uranium cake sample. This is because of a relatively high activity concentration of U in the samples resulted in the dead time of higher than 70%. The same phenomenon was observed for the measurement of Th in the thorium cake sample. For the determination of U in the thorium cake sample by the gamma-ray spectrometry, the density effect led to the underestimation of U concentration.

The concentration of U and Th in cerium and lanthanum oxide samples could not be detected by the gamma-ray spectrometry and the WDXRF techniques.
Table 2. Mean concentrations in wt% or mg kg$^{-1}$, standard deviation (SD) and coefficient of variation (CV%) for the measurement of U in the Thai monazite ore process samples by gamma spectrometry and WDXRF with different sample preparations, loose powder (LP), pressed pellet (PP) and fused bead (FB).

| Sample                                | Technique          | Element   | Mean conc. (wt%) | SD   | CV   |
|---------------------------------------|--------------------|-----------|------------------|------|------|
| Monazite                              | $\gamma$-spectrometry | U via $^{214}$Pb | 0.43             | 0.01 | 1.69 |
|                                       |                    | U via $^{214}$Bi | 0.42             | 0.01 | 2.69 |
|                                       | WDXRF (LP)         | U         | 0.47             | 0.01 | 2.18 |
|                                       | WDXRF (PP)         | U         | 0.41             | 0.01 | 4.35 |
|                                       | WDXRF (FB)         | U         | 0.41             | 0.01 | 1.62 |
| Mixed rare earth hydroxide            | $\gamma$-spectrometry | U         | nd               | -    | -    |
|                                       | WDXRF (LP)         | U         | 0.42             | 0.00 | 0.02 |
|                                       | WDXRF (PP)         | U         | 0.38             | 0.02 | 3.77 |
|                                       | WDXRF (FB)         | U         | 0.40             | 0.01 | 2.10 |
| Tri-sodium phosphate                  | $\gamma$-spectrometry | U via $^{226}$Ra | 132.44 (mg kg$^{-1}$) | 1.38 | 1.04 |
|                                       | WDXRF (LP)         | U         | 0.14             | 0.00 | 3.07 |
|                                       | WDXRF (PP)         | U         | 0.06             | 0.00 | 6.43 |
|                                       | WDXRF (FB)         | U         | nd               | -    | -    |
| Enriched cerium hydroxide            | $\gamma$-spectrometry | U via $^{226}$Ra | 22.69 (mg kg$^{-1}$) | 0.70 | 3.08 |
|                                       | WDXRF (LP)         | U         | nd               | -    | -    |
|                                       | WDXRF (PP)         | U         | nd               | -    | -    |
|                                       | WDXRF (FB)         | U         | nd               | -    | -    |
| Uranium cake                         | $\gamma$-spectrometry | U via $^{226}$Ra | 32.13             | 0.36 | 1.11 |
|                                       | WDXRF (LP)         | U         | 76.88             | 0.55 | 0.63 |
|                                       | WDXRF (PP)         | U         | 77.58             | 0.15 | 0.17 |
|                                       | WDXRF (FB)         | U         | 77.19             | 0.10 | 0.12 |
| Thorium cake                         | $\gamma$-spectrometry | U         | nd               | -    | -    |
|                                       | WDXRF (LP)         | U         | 0.49             | 0.07 | 1.07 |
|                                       | WDXRF (PP)         | U         | 0.32             | 0.06 | 0.88 |
|                                       | WDXRF (FB)         | U         | 0.43             | 0.07 | 1.13 |
| La$_2$O$_3$                           | $\gamma$-spectrometry | U         | nd               | -    | -    |
|                                       | WDXRF (LP)         | U         | nd               | -    | -    |
|                                       | WDXRF (PP)         | U         | nd               | -    | -    |
|                                       | WDXRF (FB)         | U         | nd               | -    | -    |
| CeO$_2$                               | $\gamma$-spectrometry | U         | nd               | -    | -    |
|                                       | WDXRF (LP)         | U         | nd               | -    | -    |
|                                       | WDXRF (PP)         | U         | nd               | -    | -    |
|                                       | WDXRF (FB)         | U         | nd               | -    | -    |

nd = not detected
Table 3. Mean concentrations in wt% or mg kg\(^{-1}\), standard deviation (SD) and coefficient of variation (CV\%) for the measurement of Th in the Thai monazite ore process samples by gamma spectrometry and WDXRF with different sample preparations, loose powder (LP), pressed pellet (PP) and fused bead (FB).

| Sample                  | Technique            | Element     | Mean conc. (wt%) | SD   | CV  |
|-------------------------|----------------------|-------------|-----------------|------|-----|
| Monazite                | \(\gamma\)-spectrometry | Th via \(^{228}\)Ac | 6.69            | 0.15 | 2.30|
|                         |                      | Th via \(^{212}\)Pb | 6.24            | 0.22 | 3.68|
|                         |                      | Th via \(^{212}\)Bi | 6.76            | 0.08 | 1.11|
|                         |                      | Th via \(^{208}\)Tl | 6.49            | 0.08 | 1.22|
|                         | WDXRF (LP)           | Th           | 8.44            | 0.02 | 0.19|
|                         | WDXRF (PP)           | Th           | 7.39            | 0.09 | 1.08|
|                         | WDXRF (FB)           | Th           | 7.37            | 0.05 | 0.62|
| Mixed rare earth hydroxide | \(\gamma\)-spectrometry | Th via \(^{228}\)Ac | 5.86            | 0.16 | 2.68|
|                         |                      | Th via \(^{212}\)Pb | 5.77            | 0.14 | 2.35|
|                         |                      | Th via \(^{208}\)Tl | 5.90            | 0.25 | 4.30|
|                         | WDXRF (LP)           | Th           | 9.12            | 0.04 | 0.34|
|                         | WDXRF (PP)           | Th           | 8.05            | 0.12 | 1.34|
|                         | WDXRF (FB)           | Th           | 8.69            | 0.07 | 0.67|
| Tri-sodium phosphate     | \(\gamma\)-spectrometry | Th via \(^{212}\)Pb | 0.88 (mg kg\(^{-1}\)) | 0.13 | 15.62|
|                         | WDXRF (LP)           | Th           | nd              | -    | -   |
|                         | WDXRF (PP)           | Th           | nd              | -    | -   |
|                         | WDXRF (FB)           | Th           | nd              | -    | -   |
| Enriched cerium hydroxide | \(\gamma\)-spectrometry | Th via \(^{212}\)Pb | 38.90 (mg kg\(^{-1}\)) | 1.60 | 4.12|
|                         | WDXRF (LP)           | Th           | nd              | -    | -   |
|                         | WDXRF (PP)           | Th           | nd              | -    | -   |
|                         | WDXRF (FB)           | Th           | nd              | -    | -   |
| Uranium cake            | \(\gamma\)-spectrometry | Th via \(^{228}\)Ac | 2.98            | 0.06 | 2.11|
|                         |                      | Th via \(^{212}\)Pb | 2.18            | 0.03 | 1.62|
|                         |                      | Th via \(^{208}\)Tl | 2.92            | 0.12 | 4.12|
|                         | WDXRF (LP)           | Th           | 5.39            | 0.07 | 1.07|
|                         | WDXRF (PP)           | Th           | 5.48            | 0.06 | 0.88|
|                         | WDXRF (FB)           | Th           | 5.57            | 0.07 | 1.13|
| Thorium cake            | \(\gamma\)-spectrometry | Th via \(^{228}\)Ac | 39.28           | 0.83 | 2.11|
|                         |                      | Th via \(^{212}\)Pb | 38.37           | 1.99 | 5.18|
|                         |                      | Th via \(^{212}\)Bi | 39.51           | 1.29 | 3.26|
|                         |                      | Th via \(^{208}\)Tl | 44.46           | 1.28 | 2.88|
|                         | WDXRF (LP)           | Th           | 80.02           | 0.64 | 0.71|
|                         | WDXRF (PP)           | Th           | 56.01           | 1.84 | 2.89|
|                         | WDXRF (FB)           | Th           | 75.57           | 0.73 | 0.85|
| La\(_2\)O\(_3\)         | \(\gamma\)-spectrometry | Th           | nd              | -    | -   |
|                         | WDXRF (LP)           | Th           | nd              | -    | -   |
|                         | WDXRF (PP)           | Th           | nd              | -    | -   |
|                         | WDXRF (FB)           | Th           | nd              | -    | -   |
CeO$_2$ & $\gamma$-spectrometry & Th & nd & - & - \\
& WDXRF (LP) & Th & nd & - & - \\
& WDXRF (PP) & Th & nd & - & - \\
& WDXRF (FB) & Th & nd & - & - \\
\(\text{nd} = \text{not detected}\)

4. Conclusion

Gamma-ray spectrometry technique was utilized to the determination of U and Th concentrations in the monazite ore processing samples. The results showed that there was satisfactory agreement between the gamma-ray spectrometry and the WDXRF for the U and Th measurements in the monazite ore samples. The density matrix and the dead time effects resulted in the precision and accuracy of U and Th measurements by gamma-ray spectrometry for the mixed rare earth hydroxide, the uranium cake and the thorium cake samples.

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