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Analytical Method Validation of Thorium in Ore Sample Using Uv-Vis Spectrophotometer

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ABSTRACT

Monazite contains several rare earth elements (REE) along with radioactive elements, i.e., thorium (Th) and uranium (U). Thorium content in monazite is several times higher than uranium. Monazite contains around 12% thorium oxide, but the thorium content in this mineral varies depending on location. To determine the thorium content in monazite, an appropriate and validated analytical method is needed so that the reliability of the test results can be trusted. Apart from that, method validation is one of the clauses in SNI ISO/IEC 17025:2017 that must be fulfilled by the laboratory to be certified and produce reliable data. This research aims to validate analytical methods for non-standard and modified methods that are likely to be used outside the scope. In this research, the method used to digest and analyse thorium in mineral samples refers to the ASTM E2941-14 method with several modifications. Therefore, the analysis method needs to be validated. Validation of the analytical method is carried out by testing several parameters such as linearity and working range tests, accuracy, precision (repeatability), Limit of Detection (LOD), and Limit of Quantitation (LOQ). The results of linearity, accuracy, and repeatability tests that meet the acceptance requirements can be used as a method of validation evaluation. The results of the method validation parameter test met the acceptance requirements, with the linearity test showing a coefficient of determination (R2) of 0.997, the accuracy test showing % a recovery value of 106.22%, and the precision (repeatability) test showing %RSD of 3.76% with LOD value is 0.650 mg/L, and LOQ is 0.724 mg/L. Based on the results of these parameter tests, the method for analysing thorium in mineral samples was validated.

Keywords: monazite, minerals, thorium, validation method

INTRODUCTION

Thorium is a radioactive element with high strategic value because it can be used as nuclear fuel [1]. Like all radioactive minerals, thorium has certain risks, such as contamination by radiation exposure. However, thorium is safer and less hazardous than other radioactive materials like uranium and plutonium since it is not fissile, meaning it cannot start a chain reaction on its own [2]. Thorium is abundant in nature, one of which is contained in the monazite. One of the by-products of mining cassiterite tin ore on the island of Bangka is monazite. Monazite contains several rare earth metal elements (REE) along with radioactive elements such as thorium (Th) and uranium (U). In monazite, the thorium content is several times greater than uranium [3],[4]. Monazite contains around 12% thorium oxide, but the thorium content in this mineral varies depending on location [5].

There are some procedures to determine thorium in a sample. Conventional analytical procedures use radiation and radiochemical techniques [6]. Generally, thorium analysis is conducted using the radiometric method (e.g., alpha spectrometry). In spite of the fact that the methods using alpha and gamma spectroscopy are effective, too low or high concentrations of the sample result in poor data [7]. Recently, analysing thorium using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which could read trace to high concentrations of elements, has appeared to have excellent precision, accuracy, and sensitivity and has been widely used to analyse natural radionuclides and their isotopic ratios [8]–[12]. Analysing thorium using a spectrophotometer UV-Vis is rarely used. Therefore, that method has to be validated in order to produce reliable data.

Testing using a validated analytical method is required to determine the thorium content in monazite, which is done in a laboratory certified by SNI ISO/IEC 17025:2017 so that the reliability of the test result can be trusted. Data from testing laboratory tests that apply SNI ISO/IEC 17025-2017 regulations are valid with good precision and accuracy [13]. Validation of analytical methods is one of the clauses that must be fulfilled in the requirements of the SNI ISO/IEC 17025:2017 standard and needs to be done by laboratories for non-standard and modified methods that are likely used outside the scope [14]. In this study, the method used to destroy and analyse thorium in mineral samples refers to the ASTM E2941-14 method with several modifications. Therefore, it is necessary to validate the analytical method to produce reliable test result data. Validation of the analytical method is carried out by testing several parameters such as linearity and working range tests, accuracy, precision (repeatability), Limit of Detection (LOD), and Limit of Quantitation (LOQ). The results of linearity, accuracy, and repeatability tests that meet the acceptance requirements can be used to evaluate the validation method [15].

THEORY

Validation of analytical methods is an evaluation of specific parameters based on laboratory tests to show that certain parameters have met the requirements for their use [16]. Testing laboratories must validate analytical methods for non-standard and modified methods that are likely used outside the scope designed/developed by the laboratory, standard methods used outside their intended scope, and modified standard methods to confirm their suitability. Validation must be under the specified application requirements or field of application [14]. The parameters tested in method validation are linearity and working range, the limit of detection (LOD), the limit of quantification (LOQ), accuracy, and precision [15].

Linearity and Working Range. Linearity is the ability of an analytical method to provide a proportional response to the concentration of the analyte in the sample [16]. Linear regression analysis can be seen from the calibration curve between concentration and absorbance, which is expressed in the equation:

$$Y = bx + a \tag{1}$$

The relationship of analyte response is said to be proportional when the coefficient of determination (R^2) > 0.997 [17]. While the working range is the lowest and highest limits of an analyte that are determined with acceptable accuracy, precision, and linearity [18], the working range is selected when the lowest and highest analyte concentration measurement values have a coefficient of determination (R^2) value closest to 1 [17].

The limit of Detection (LOD) or Method Detection Limit (MDL) is the most negligible concentration of an analyte in a sample that can be identified. Based on Quick Reference 2- Limit of Detection (LOD) in the Eurahem Guide Document, LOD can be expressed with the formula [15]:

$$\mathrm{SD} = \sqrt{\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}}(\mathrm{xi}-\bar{\mathrm{x}})^2}{n}} \quad (2)$$

$$LOD = \bar{X}m + 3SD \quad (3)$$

The limit of quantification (LOQ) is the most negligible concentration of analytes that can be measured with measurement uncertainty (acceptable precision and accuracy). Based on Table A3. Recommendation for Evaluation from AOAC, LOQ can be determined by the formula [19]:

$$LOQ = \bar{X}m + 5SD \quad (4)$$

Accuracy is a measure that shows the degree of closeness of the analysis results to the actual analyte levels [17]. Test accuracy using CRM can be determined by calculating % bias and % recovery (% Recovery) [15]. Bias (b) and % bias (%b) and % recovery (%R) are expressed in the following formula:

$$\%b = \frac{\bar{X}-X_{ref}}{X_{ref}}\ x\ 100 \quad (5)$$

$$\%\ \mathrm{R} = \frac{\bar{\mathrm{X}}}{\mathrm{X_{Ref}}} \times 100\% \quad (6)$$

Precision (repeatability) is the thoroughness of a method if it is carried out repeatedly by the same analyst in a short time interval [17]. Based on Table A4. Expected precision (repeatability) as a function of analyte concentration from AOAC is that an analyte with a concentration of 100–1000 mg/L meets the acceptance requirements if it has a %RSD value of 3.7–5.3%. Meanwhile, based on CV Horwitz calculations, the precision value is acceptable if the %RSD is between 0.5 CV Horwitz and 0.67 CV Horwitz [19]. Horwitz's % RSD and CV are expressed as follows:

$$\mathrm{SD} = \sqrt{\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}}(\mathrm{xi}-\bar{\mathrm{x}})^2}{n}} \quad (7)$$

$$\%\mathrm{RSD} = \frac{\mathrm{SD}}{\bar{\mathrm{X}}} \times 100\% \quad (8)$$

$$CV\ Horwitz = 2^{(1-0{,}5\log C)} \quad (9)$$

METHODOLOGY

The specifications for the chemicals used in this research are analytical grade, including aqua bidest, HNO_3 65% (Merck), $HClO_4$ 72% (Merck), HF 40% (Merck), HCl 36% (Merck), Ascorbic acid (Merck), Thorin (Merck), Th 1000 mg/L standard solution (Inorganic Ventures), Certified Reference Materials (OREAS 464).

The UV-visible spectrophotometer instrument (UVViS) is used to analyse the samples. The spectrophotometer type is Shimadzu UV-2600.

The thorium standard samples were prepared in various concentrations. The standard series solution was prepared with a concentration of 2 mg/L; 5 mg/L; 10 mg/L; 20 mg/L; 100 mg/L; 200 mg/L of standard Thorium solution 1000 mg/L. Then, 5% ascorbic acid solution and 0.1% thorin solution were added sequentially and measured using HCl pH 0.8 to 50 mL.

Specific activities were conducted to determine thorium levels. 0.5 g of CRM 464 sample was digested on a hotplate using an acid mixture consisting of aqua bidest, 65% HNO_3, 72% $HClO_4$, and 40% HF with a ratio of 10:10:10:5. The residue was dissolved with 50% HNO_3 20 mL, then measured using aqua bidest into a 25 mL measuring flask [20]. 5 mL of the prepared sample was pipetted, 5%

ascorbic acid solution and 0.1% Thorin solution were added sequentially and then measured using HCl pH 0.8 to 50 mL.

The analytical method for determining thorium is based on the modified ASTM E2941-14 standard. Acceptance requirements include linearity, the limit of detection (LOD), the limit of quantification (LOQ), accuracy, and precision [15].

The linearity and working range test were carried out by measuring a standard series solution of thorium at a concentration of 2–200 mg/L. Statistically, the regression, slope and intercept were calculated [15].

The limit of detection (LOD) and the limit of quantitation (LOQ) were obtained from a total of 7 blank sample solutions. The samples were measured once, then the standard deviation was calculated [15].

The accuracy and precision tests were using a total of 7 CRM sample solutions. These samples were prepared and measured once. Then, the bias and recovery values were calculated [19]

RESULTS AND DISCUSSION

The digestion method refers to ASTM E2941-14, which uses four-acid digestion and adds tartaric acid to the dilution. However, in this research, the analysis method was modified. Modifications to this method include eliminating the addition of tartaric acid at the dilution preparation stage and adding the 0.1% Thorin complex.

The calibration curve for the thorium standard series at concentrations of 2–200 mg/L is shown in Figure 1. The graph in Figure 1 shows the linear relationship between concentration and the instrument response, resulting in a coefficient of determination (R^2) = 0.9997, so the relationship between concentration and tool response is proportional and meets the acceptance requirements because $R^2 > 0.997$. The working range of analytes is in the lowest analyte concentration range of 2 mg/L and the highest concentration of 200 mg/L.

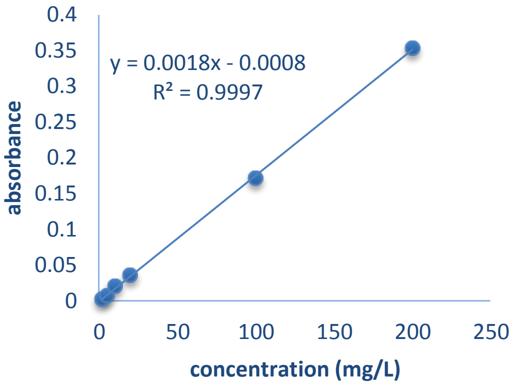

Figure 1. A thorium calibration curve with the range of 2–200 mg/L

The LOD and LOQ values can represent the sensitivity of a method by measuring blank samples. The results of measuring blank samples using this method can be seen in Table 1. The blank sample measurement data showed that the detection limit of the method stated in LOD was 0.650 mg/L, meaning that the UV-Vis spectrophotometer still provided a significant response at this thorium concentration. Meanwhile, the lowest concentration of analyte that still meets the careful and thorough criteria is represented by the LOQ value, 0.724 mg/L.

Table 1. Blank Sample Measurement Result

Sample Number	Respond (abs)	Average concentration (mg/L)
1	0.0001	0.532
2	0.0001	0.53
3	0.0001	0.517
4	0.0001	0.569
5	0.0001	0.594
6	0.0001	0.557
7	0.0001	0.482
	$\bar{X}m$	0.540
	SD	0.037
	LOD (MDL)	0.650
	LOQ	0.724

Accuracy test using Certified Reference Material (CRM) OREAS 464 resulted in data on % bias and % recovery, shown in Table 2. From these data, it was found that the % recovery obtained was 106.22%, with acceptance requirements between 90–107%, then the % recovery of the analyte met the acceptance requirements set by AOAC.

Table 2. Measured CRM Concentration Data

Sample Number	Respond (abs)	Average concentration (mg/L)
1	0.095	545.27
2	0.091	523.27
3	0.096	552.21
4	0.096	551.16
5	0.095	544.3
6	0.096	548.77
7	0.087	497.35
	$\bar{X}$	537.48
	$\bar{X}$ CRM	506
	% b (bias)	6.22
	% Recovery	106.22
	Acceptance %Recovery	90

The precision test in the analysis method using CRM produces a precision value represented by the % RSD value. Precision measurement results data are displayed in Table 3. The precision measurement data resulted in a % RSD value of 3.7605. Based on the acceptance requirements by AOAC, the % RSD method in this study meets the acceptance requirements because the % RSD is in the range of 0.5 CV Horwitz - 0.67 CV Horwitz and is also in the required % RSD range of 3.7–5.3%.

Table 3. Precision Measurement Results Data

Sample Number	Respond (Abs)	Measured concentration (mg/L)
1	0.095	545.27
2	0.091	523.27
3	0.096	552.21
4	0.096	551.16
5	0.095	544.3
6	0.096	548.77
7	0.087	497.35
	$\bar{X}$	537.48
	SD	20.21
	RSD	0.0376
	% RSD	3.76
	CRM concentration (mg/L)	506
	Concentration fraction CRM	0.000506
	Log C	-3.2958
	0.5 log C	-1.6479
	1-0.5log C	2.6479
	CV Horwitz	6.2677
	0.5 CV Horwitz	3.13
	0.67 CV Horwitz	4.18
	Acceptance	0.5 CV Horwitz < % RSD metode < 0.67 CV Horwitz %RSD = 3.7–5.3%

CONCLUSION

The results of linearity, accuracy and precision parameter tests have met acceptance requirements. The thorium analysis method in mineral samples in this study was validated with an LOD value of 0.650 mg/L and LOQ of 0.724 mg/L.

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