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Validation of The Gravimetry Method for Determining Rare Earth Elements Oxides

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ABSTRACT

The demand for minerals to meet technological developments is increasing, including minerals that contain rare earth elements (REE). The levels of REE in solids can be determined using conventional analysis methods (gravimetry) and instruments. Even though the instrument method provides more accurate results with a small amount of analyte, the cost is higher compared to the gravimetric method, which requires more analyte and provides good results. Therefore, the gravimetric method is a solution for areas with limited instruments and budgets. The study aims to validate the gravimetric method for determining REE oxides levels, evaluate its precision and accuracy, and assess its feasibility of use. In this study, two methods were used for REE analysis: the ASTM E2941-14 method with sample weight modification and the addition of acid to increase REE oxides recovery and a precipitation method using oxalic acid. The validation stages include sample dissolution, precipitation, filtration, and ash-making. The research results show that the RSD value is 0.3154, which is smaller than 2/3 of Horwitz's CV, namely 4.1727, which means it meets the precision acceptance requirements of ISO/IEC 17025:2017. The REE oxides recovery value, which indicates accuracy, also increased to 97.74%. Therefore, the gravimetric method can be used as an alternative for determining REE oxides levels.

Keywords: gravimetric methods, method validation, oxalic acid, REE oxides

INTRODUCTION

The need for minerals has increased significantly along with rapid technological developments. Industry and technological development depend on minerals as raw materials for energy sources, including rare earth elements (REE). REE have a very high economic value because they are essential for various current technologies. Their contributions to modern society are significant, as they facilitate progress in sustainable energy and digital innovation. The relevance of REE is emphasized in literature like the MRS Bulletin, which explores the economic aspects of these minerals and their crucial role in ensuring a stable supply and managing market fluctuations. This highlights their strategic significance in the global economy [1]. REE plays a crucial role in advancing materials technology in numerous disciplines. For example, high-purity Dy is a TLD crystal dopant that protects radiation workers. Dysprosium is a lustrous, metallic element that is infrequently used in its pure metal state because of its pronounced reactivity with water and air. Dysprosium is frequently employed in NdFeB permanent magnets to mitigate demagnetization at elevated temperatures. These magnets are used in electrical devices, wind turbines, and electric cars [2]. Additionally, the potential for recycling REE from end-of-life electric vehicles has been widely highlighted, further emphasizing their economic and ecological value in today's society [3].

REE resources can be found in several types of deposits. The primary form of REE is a by-product of iron ore mining, while the secondary form can be alluvial and lateritic deposits. Some of the main REE-containing minerals include bastnaesite, monazite, xenotime, and apatite.

Two methods are commonly used to determine REE content in solids: the analysis method using spectrophotometry with an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument and the gravimetric method. These two methods have two different purposes. The analysis method uses spectrophotometry with an ICP-OES device to determine each REE concentration. Meanwhile, the gravimetric method aims to determine the oxide content of REE.

Both methods have their respective advantages. The analysis method using ICP-OES has several advantages. ICP-OES can identify and measure all and each element present in the sample simultaneously in a relatively short time. Meanwhile, the gravimetric method only requires relatively simple and cheap equipment. As for the drawbacks, the analysis method using ICP-OES is expensive, while the gravimetric method takes longer.

It is also essential to consider the availability and cost of equipment in the laboratory. Several studies have reported that oxalic acid is used as a precipitant for REE oxides[4]–[6]. However, there has been a shortage of validation for this particular approach. The originality of this research lies in the methodology used to dissolve solid materials, as well as the subsequent validation of the technique, which establishes a new benchmark in the field. In certain conditions and facilities that do not have access to laboratories with adequate instrument equipment, gravimetric methods can be a more practical solution at a lower cost. The solid sample containing REE is digested using the four-acid digestion method from ASTM E2941-1 to determine the REE oxides content. The REE oxides are precipitated with oxalic acid, and the resulting product is ash.

Several modifications are made in the four-acid digestion method from ASTM E2941-14. Therefore, validation of the gravimetric method was carried out to assess whether the results provided by this method could be considered appropriate or not. Based on ISO/IEC 17025:2017 clause 7.2.1, Testing Laboratories must use appropriate and valid methods and procedures [7]. This validation aims to compare the precision and accuracy values obtained from the gravimetric method with the values determined as standard requirements. In validating this method, Certified Reference Material (CRM) is used as a reference to compare the REE oxides content obtained.

Method Validation

Based on ISO/IEC 17025:2017, method validation is essential in chemical analysis. Laboratories must validate non-standard, laboratory-developed, standard methods used outside the scope, amplification, and modified standard methods to confirm whether the method is suitable for the intended use [7]. The validation parameters used are accuracy and precision using a sample in the form of CRM Oreas 464. CRM is a material that has traceable, homogeneous and stable material properties. Therefore, CRM is usually used to calibrate equipment, validate methods, estimate accuracy, estimate precision, and develop test methods [8].

METHODOLOGY

This research was conducted at the Research Center for Nuclear Fuel Cycle and Radioactive Waste Technology. The methods used to determine REE oxide content are the four-acid digestion methods from E2941-1 and the gravimetric method. The working details are described as follows:

Materials

The specifications for the chemicals used in this research are analytical grade Oxalic Acid 10%, Nitric Acid, Perchloric Acid, Hydrofluoric Acid, Hydrochloric Acid, CRM Oreas 464, and Aquades.

Instruments

The instruments used in this research are a hot plate, furnace, oven, analytical balance, PTFE beaker, measuring cup, dropper pipette, Whatman 42, porcelain cup and 25mL PTFE volumetric flask.

The four-acid digestion

The four-acid digestion method is used for dissolving the solid sample. The four-acid digestion method from ASTM E2941-14 has undergone several modifications. First, the number of samples weighed was 2±0.01 grams. Second, the volume of the destruction reagent was also changed to double. Third, in the process of dissolving the sample, it is dissolved in a 25 mL PTFE volumetric flask. Five samples of CRM oreas 464 were weighed 2 grams and put into a PTFE Beaker. Then, distilled water, nitric acid, perchloric acid, and hydrofluoric acid were added with a modified volume of twice as much as recommended in ASTM E2941-14. Next, the sample was heated using a hot plate to a temperature of 200^{o}C in a fume hood until dry. After drying, the remaining sample was added with hydrochloric acid and transferred into a 25 mL PTFE volumetric flask.

Precipitation

The sample solution, as much as 10 mL, was taken and then conditioned until the pH reached pH 2 using diluted NaOH. Next, the sample solution was precipitated with 10% oxalic acid and left overnight to reach optimal conditions (Fig. 1). After that, the residue was filtered using the Whatman 42 filter paper. Next, the residue was washed with 2% oxalic acid and oven until dry (Fig. 2).

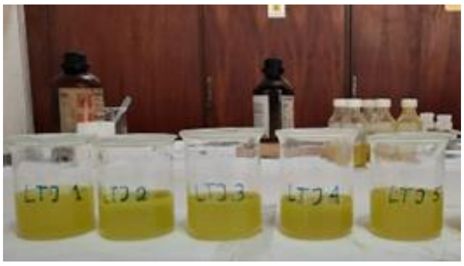

Figure 1. Precipitation of REE oxide using oxalic acid

Figure 2. CRM Oreas 464 sample after drying

Ash-making

The residue was put into a porcelain cup, which was previously weighed empty. Next, the porcelain cup containing the sediment is ashed using a furnace at a temperature of 1000^{o} C. After ash-making, the cup is cooled and weighed. The process is repeated until a fixed and stable weight is obtained.

Figure 3. The treated sample after ash-making

Precision and Accuracy

After five repetition measurements of the sample, the weight of the ashing result and the weight of the porcelain cup were obtained. Implementing repeatability, or performing 5 to 7 repetitions during the validation of analytical methods, is critical because it ensures that the technique provides consistent and reproducible results under the same conditions [11]. The data was used to calculate the ash weight as below.

$$W_{ash} = W_{heating} - W_{container} \quad (1)$$

W_{ash} is the weight of the ash (g), $W_{heating}$ is the weight of the ash product (g), and $W_{container}$ is the weight of the empty porcelain cup (g). The REE concentration (g/mL) was then calculated:

$$C_{REE} = \frac{W_{ash} x\, F_P}{W_{sample}} \quad (2)$$

F_p is the dilution factor, and W_{sample} is the sample weight (g). Then, the REE concentration value was converted to mg/L. The value of standard deviation (SD) was calculated [12]:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}} \quad (3)$$

SD is the standard deviation, x_i is the i data, $\bar{x}$ is the average, and n is the amount of data. Then, the coefficient of variation (RSD) can be determined [12]:

$$RSD = \frac{SD}{\bar{x}} \quad (4)$$

$CV\ Horwitz$ is the evaluation of deviation tolerance, RSD is the coefficient of variation, and C is the reference concentration. Compare the RSD value with 2/3 of the $CV\ Horwitz$ value. If the RSD value is smaller than the $CV\ Horwitz$ value, the analysis results meet the specified precision requirements [13].

$$CV\ Horwitz = 2^{1-0.5\log C} \quad (5)$$

Accuracy is calculated from the recovery value, where R is recovery, $\bar{x}$ is the average data, and x_{ref} is the reference value [14].

$$R(\%) = \frac{x}{x_{ref}} x\ 100 \quad (6)$$

The recovery value was compared with the table of accuracy acceptance conditions in Table 1 [12].

Table 1. Analyte recovery based on analyte concentration

Analyte, %	Mass fraction (C)	Unit	Mean recovery, %
100	1	100%	98-102
10	10^{-1}	10%	97-103
1	10^{-2}	1%	95-105
0.1	10^{-3}	0.1%	90-107
0.01	10^{-4}	100 ppm	80-110
0.001	10^{-5}	10 ppm	
0.0001	10^{-6}	1 ppm	
0.00001	10^{-7}	100 ppb	
0.000001	10^{-8}	10 ppb	60-115
0.0000001	10^{-9}	1 ppb	40-120

RESULTS AND DISCUSSION

The use of ASTM E2941-14 for REE destruction is limited to analyses performed with ICP-OES and AAS instruments [15]. Adjustments need to be made in the form of modifications to carry out gravimetric analysis. Modifications are needed to increase the recovery of REE oxide compounds using the gravimetric method. Modifications include increasing the sample weight and increasing the solvent volume [16]. Table 2 presents the results of modification experiments carried out by the laboratory. Modifications were implemented based on the results of the REE oxides content, as presented in Table 2. The CRM Oreas 464 sample was weighed at a mass of two grams and added twice the volume of acid.

Table 3 presents the results of acid modification in the ASTM E2941-14 method and the precipitation method with oxalic acid, which show the success of increasing the recovery of REE oxides at pH 2. This follows previous research, which showed that REE oxides will form and precipitate optimally at pH 2 [4]–[6], [17]. The pH level of the solution has a significant effect on how well REE oxides are deposited and recovered [17], [18]. Therefore, it is necessary to control the pH of the solution at pH 2 using a pH meter. At pH 2, oxalic acid is in the form of an oxalate ion ($C_2O_4^{2-}$), a negative ion that can form a complex with REE (RE^{3+}). The following is the REE oxides precipitation reaction [17]:

$$2RE^{3+} + 3H_2C_2O_2 + 10H_2O \leftrightarrow 2RE_2(C_2O_4)_3.10H_2O \downarrow + 6H^+ \quad (7)$$

The REE oxides concentration on the Oreas 464 certificate is 51058.88 mg/L or 0.0510 g/mL [19]. So, precision and accuracy calculations were carried out, presented in Tables 4 and 5.

Table 2. The result of modification experiments

Sample (gram)	Ignition weight (gram)	Container weight (gram)	Ash weight (gram)	REE oxides concentration (g/mL)
Following ASTM E2941-14 procedures:				
0.5001	19.8259	19.8159	0.0100	0.0125
0.5003	18.4415	18.4290	0.0125	0.0156
Modification of the amount of sample weight and acid:				
1.0012	18.4266	18.3993	0.0273	0.0302
1.0015	19.4960	19.4718	0.0242	0.0341
2.0012	19.5304	19.4898	0.0406	0.0508
2.0016	18.6824	18.6432	0.0392	0.0490

Table 3. Data of REE oxide concentration (g/mL)

Sample (gram)	Ignition weight (gram)	Container weight (gram)	Ash weight (gram)	REE oxide concentration (g/mL)
2.0019	20.9145	20.8744	0.0401	0.0500
2.0025	19.4988	19.4589	0.0399	0.0498
2.0021	19.4150	19.3752	0.0398	0.0497
2.0025	19.8563	19.8165	0.0398	0.0497
2.0026	20.6190	20.5791	0.0399	0.0498

Table 4. The gravimetry method precision calculation

Precision	
Reference Material Value (g/mL)	0.0511
X (g/mL)	0.0498
SD	0.0002
RSD	0.3154
1-0,5 CV Horwitz	2.6460
2/3 CV Horwitz	4.1727
RSD < 2/3 CV Horwitz	0.3154 < 4.1727

Table 5. The gravimetry method accuracy calculation

Accuracy	
X (g/mL)	0.0498
Reference Material Value (g/mL)	0.0511
Recovery	97.57%

The RSD value is <2/3 CV Horwitz, meaning the precision value is very good and meets the acceptance requirements of ISO/IEC 17025:2017 [13]. This value indicates that the resulting data is consistent or has minor variations. The RSD value measures the deviation from a data set, while CV Horwitz is an empirical model used to predict variations based on analyte concentration. Meanwhile, the recovery value in the accuracy calculation also meets the acceptance requirements of ISO/IEC 17025:2017 of 97.57%, which means it is between 97%–103% [12]. Then, the precision and accuracy calculations of the ICP-OES method are carried out, which are presented in Tables 6 and 7.

Table 6. The ICP-OES method precision calculation

Precision	
Reference Material Value (g/mL)	0.0511
X (g/mL)	0.0484
SD	0.0004
RSD	0.8958
1-0,5 CV Horwitz	2.6458
2/3 CV Horwitz	0.2130
RSD < 2/3 CV Horwitz	0.8958 > 0.2130

Table 7. The ICP-OES method accuracy calculation

Accuracy	
X (g/mL)	0.0484
Reference Material Value (g/mL)	0.0511
Recovery	94.74%

If the REE oxides measurements are compared with the precision and accuracy values obtained using the ICP-OES method, the gravimetric method is still superior. This is demonstrated in Tables 6 and 7, where the RSD value is >2/3 CV Horwitz, indicating that it does not meet the acceptance requirements. Apart from that, the accuracy value also does not meet the acceptance requirements because the recovery value is only 94.74%.

This happens because each method has limitations. The gravimetric method is superior to measuring the REE oxides as a whole and cannot measure the REE oxides of individual elements. Meanwhile, the ICP-OES method, on the other hand, is superior in measuring the REE oxide of each element, and several REE oxides elements cannot be measured due to the Limit of Detection (LOD).

CONCLUSION

The study of the gravimetry method validation of determining REE oxides content meets the accuracy and precision acceptance requirements specified by ISO 17025:2017. In conclusion, the gravimetry method can be a more economical alternative because it is declared valid. The gravimetric method can also be a more practical and cost-effective alternative.

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