Method validation for determination of some rare-earth elements in rice using ICP-MS

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Abstract. In the present work, an inductively coupled plasma mass spectrometer operating in single quadrupole was performed for determination of some rare-earth elements including La, Sm, Eu, Tl, and U in rice. The samples were prepared by microwave digestion with nitric acid. The fortifications of rice samples at 3 levels were studied in order to check the accuracy of the proposed method. The experiment was performed under the internal standard method with the coefficient of determination higher than 0.9990. The average recoveries of all elements were higher than 92% with the standard deviation less than 4.5.

1. Introduction

Rare earth elements (REEs) are members of Group IIIA in the Periodic Table and have similar physical and chemical properties [1]. The REEs are frequently subdivided into three groups: the light (lanthanum to europium), middle (samarium to holmium) and heavy REEs (gadolinium to lutetium). Information about the contents of rare-earth elements (REEs) in several kinds of samples is very important in geochemical, biochemical and environmental studies. In addition, nowadays REEs have been widely used in agriculture as a trace element fertilizer in all over the world. Therefore, the need for accurate trace analysis of REEs in environmental samples has increased. Because the content of REEs in environmental samples such as rice is generally very low, it is very difficult to determine them accurately by conventional analytical methods.

Owing to very low REE concentrations and the complex matrix, sophisticated analytical techniques have been developed for the determination of trace REEs in environmental, biological, and food samples, such as neutron activation analysis (NAA) [2–4], X-ray fluorescence (XRF) [5], isotopic dilution mass spectrometry (IDMS) [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7–9], and ICP-MS [10]. Among these techniques, XRF suffers poor detection limits for REEs, which limit its application for REE detection in real samples. NAA is sensitive but requires access to a nuclear reactor, so it is not suitable for routine REE analysis. Although the IDMS assay allows fast and multi-elemental determination of REEs, the detection limit for REEs is still 2–3 orders of magnitude poorer than with ICP-MS.

In this study, we investigated the method validation for the determination some rare-earth elements including Lanthanum (La), Samarium (Sm), Europium (Eu), Thallium (Tl), and Uranium (U) in rice using inductively coupled plasma mass spectrometry with microwave digestion. The measurement was performed by internal standard method.
2. Materials and methods

2.1. Sample collection and preparation
Thai rice samples were dried in a hot-air oven at 60 °C for 48 hours and kept in desiccator prior to analysis. The powdered rice samples (0.8 g) were weighed into 100 mL TFM vessels. After samples were spiked with the rare-earth standards at three concentration levels (0.1, 1, and 10 mg/kg), 10 mL of 60% HNO₃ was then mixed in 100 mL closed TFM vessel. The closed vessels were placed for digestion in a Mars™ 6 Xpress microwave digestion system (CEM, NC, USA). The following digestion program was created at 15-min ramp and 30-min hold at 950 W. After cooling down to room temperature, all digested solutions were filtered through a 0.45 µm syringe filter. The sample solution was heated to dryness and reconstituted in 10 mL of 2% (V/V) HNO₃ prior to analysis by inductively coupled plasma mass spectrometer (ICP-MS).

2.2. ICP-MS Analysis
All measurements were determined using an ICP-MS (Agilent 7900, Agilent Scientific Technology Ltd., USA). ICP-MS analyses were carried out with an internal standard calibration approach. Each solution was measured in triplicate. The operating conditions of ICP-MS instrument are shown in table 1.

Table 1. Operating conditions for ICP-MS.

| ICP-MS parameters | Condition       |
|-------------------|-----------------|
| RF power         | 1550 W          |
| Nebulizer Pump  | 0.1 rps         |
| Sampling depth   | 8.0 mm          |
| Carrier gas      | 0.8 L min⁻¹     |
| Makeup gas       | 0.15 min⁻¹      |

3. Results and discussion
The results of method validation of ICP-MS technique for the analysis of REEs in rice are shown in table 2. The standard calibration plots of REEs are presented in figure 1. The least square linear regression equations of La, Sm, Eu, Tl, and U were $y = 0.164x - 0.000007$, $y = 0.029x - 0.00003$, $y = 0.109x - 0.0002$, $y = 0.189x - 0.0005$, $y = 0.247x - 0.0004$, respectively, which x refers to concentration of each element and y refers to the ratio between CPS of standard and CPS of internal standard. Good linearity was obtained with the correlation coefficient ($R^2$) greater than 0.9997 for each element. The limits of detection (LODs) were 0.010, 0.0007, 0.008, and 0.009 µg L⁻¹ for La, Sm, Eu, Tl, and U, respectively. Limits of quantitation (LOQs) were in the range of 0.016 to 0.020 µg L⁻¹. The analytical figures of merit are summarized in figure 1. The relative standard deviations (%RSD) of the measurements of REEs ranged from 1.4% to 5.1% which was satisfied for the purpose of this work. The spiked recoveries of the REEs in rice at three concentration levels (0.1, 1, and 10 mg/kg) are presented in table 3. The recoveries of La, Sm, Eu, Tl, and U at the spiked concentration of 0.1 mg/kg were 88.03, 95.75, 93.59, 99.56, and 97.92%, respectively. The recoveries of La, Sm, Eu, Tl, and U at the spiked concentration of 1 mg/kg were 92.94, 94.84, 94.21, 100.48, and 100.24%, respectively. The recoveries of La, Sm, Eu, Tl, and U at the spiked concentration of 10 mg/kg were 96.93, 94.59, 92.58, 98.61, and 94.50%, respectively. Good accuracy of the method was achieved with high average recoveries (92.6-99.6%). Regardless to La, no concentration effect that related to the recovery was obtained.
Figure 1. Internal standard calibration plots of La, Sm, Eu, Tl, and U.
Table 2. Analytical figures of merit for the determination of rare-earth elements.

| Element | Working range (μg/L) | R²    | %recovery | %RSD | LOD (μg/L) | LOQ (μg/L) |
|---------|----------------------|-------|-----------|------|------------|------------|
| La      | 0.025-0.250          | 0.9999| 92.64     | 5.1  | 0.010      | 0.019      |
| Sm      | 0.025-0.500          | 0.9998| 95.06     | 2.1  | 0.007      | 0.017      |
| Eu      | 0.025-0.250          | 0.9998| 93.46     | 2.6  | 0.007      | 0.016      |
| Tl      | 0.025-1.000          | 1.0000| 99.55     | 1.4  | 0.008      | 0.020      |
| U       | 0.025-0.250          | 0.9999| 97.55     | 3.2  | 0.009      | 0.019      |

Table 3. Percentage of recovery for the studied REEs in rice.

| Element | %recovery 0.1 mg/kg | %recovery 1 mg/kg | %recovery 10 mg/kg | Average |
|---------|----------------------|-------------------|--------------------|---------|
| La      | 88.03                | 92.94             | 96.93              | 92.64   |
| Sm      | 95.75                | 94.84             | 94.59              | 95.06   |
| Eu      | 93.59                | 94.21             | 92.58              | 93.46   |
| Tl      | 99.56                | 100.48            | 98.61              | 99.55   |
| U       | 97.92                | 100.24            | 94.50              | 97.55   |

4. Conclusion
The proposed method gave linear calibrations in the range of 0.025–1.0 μg/L with correlation coefficients greater than 0.9997. Limits of detection (LODs) and limits of quantitation (LOQs) were 0.007–0.010 μg/L and 0.016–0.020 μg/L, respectively. Good precision was achieved with relative standard deviation lower than 6%. High accuracy, with the average recoveries higher than 92% was obtained. The proposed ICP-MS with microwave digestion has shown to be of high potential for the analysis of some rare-earth elements including Lanthanum (La), Samarium (Sm), Europium (Eu), Thallium (Tl), and Uranium (U) in rice.

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