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Determination of Some Rare Earth Elements, Th, and U in Vegetable using Inductively Coupled Plasma Mass Spectrometry

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Determination of some rare earth elements (La, Ce, Sm, Eu, and Gd), Th, and U in lettuce was investigated. The elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Good precision for the determination of the elements was achieved. Method validation of the proposed method was performed using NIST SRM 1573a-Tomato Leaves and NIST 1570a-Trace Elements in Spinach Leaves certified reference materials. In this study, the certified reference materials and lettuce samples were acid-digested using microwave digestion system prior to analysis by ICP-MS. The recoveries of all elements were in the range 78.2% – 100.0%. The repeatability and intermediate precisions were less than 5% and 9%, respectively. The determination of La, Ce, Sm, Eu, Gd, Th, and U concentrations in some lettuce samples was also investigated.

Keywords: Rare earth elements; Thorium; Uranium; ICP-MS; lettuce

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As urbanization and industrialization have raised without environmental impact concerns, several noxious elements from industries, mining, and agriculture are being discharged [1]. There is fear that the exposure of these elements is harmful to human health and accumulating at different levels in food chain. It has been reported that plants grown in contaminated soils are possible to assimilate and accumulate the harmful elements in different plant tissues [1-2]. Thus, the uptake of the harmful elements cannot be prevented by plants. Some metals tend to accumulate in different body tissue such as bones, muscle, and liver, poisoning to human health [3].

Rare earth elements (REEs) are group of lanthanides including lanthanum (La) to lutenium (Lu) and scandium (Sc) and yttrium (Y), with similar chemical and physical properties. REEs are exploited in several sectors, e.g. alternative energy storage, electro-thermal hybrid vehicles, electronic devices, and agriculture [1]. Despite the utilization, little attention is paid to them as the emerging pollutants and their related environmental risk. REEs are generally present in low concentrations in atmosphere, soil, water, and plants. However, REEs can be accumulated in such environments according to anthropogenic processes [4]. Since last decade, there have concerned because of their persistence properties in environments [5-7] and bioaccumulate in biota [8]. Although there are no incidents of human poisoning through food chain have been reported, potential concerns regarding the impact of continuous exposure to low levels of REEs on health risk have been increasing because of their accumulation in bones, blood, and brain [9]. In pervious study, it has found that long-term exposure to REEs may lead to human problems such as liver function decline [10]. Long-term consumption of food contaminated with REEs may result in chronic and poisoning. However, low concentrations of REEs have some beneficial aspects for biochemical and physiological responses of animals and plants [11]. They are also widely used in plant regulators for crops and feed additives in poultry, livestock, and agriculture. REE from natural environment and agriculture are consequently presented in agricultural products ingested by humans through the food chain. Therefore, it is necessary to investigate the concentrations of REEs in daily food or major foods [11] such as freshwater [12], seafood [12], rice [1, 2, 8, 11, 12], fruits [11-13], and vegetables [2, 4, 9, 11-15] in order to access the potential risk of REEs to human health. Normally, the levels of REEs in foods are very low (ppt). In order to determine the elements at such concentrations, the most sensitive analytical techniques are required. One of the most powerful techniques to determine REEs in biological samples is inductively coupled plasma mass spectrometry (ICP-MS) because it is capable to carry out multi-element analysis with relatively low detection limits.

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In this study, we investigated a method for the determination of some REEs (La, Ce, Sm, Eu, and Gd), Th, and U in lettuce using ICP-MS and closed vessel microwave digestion methods. The advantages of microwave digestion method are high efficiency, fast digestion, low environmental pollution, safe and efficient analytical procedure. The measurement was performed by internal standard method. The procedure was validated using two matrix certified reference materials (CRMs). The method was also applied for the determination of some REEs, Th, and U in real sample, lettuce samples. Moreover, the dataset provided the information on the distribution of some REEs, Th, and U concentrations in lettuce. The obtained dataset can also be applicable to estimate the intake of some REEs, Th, and U via vegetables.

EXPERIMENTAL

Chemicals and Materials

Ultrapure water (resistivity of 18.2 MΩ cm), used for materials cleaning and solution preparation, was purified by a Milli-Q water purification system (Millipore, Burlington, MA, USA). Nitric acid (HNO_3), trace metal grade and suprapur hydrogen peroxide (H_2O_2) were obtained from Fisher Chemical and Merck (Darmstadt, Germany), respectively. Lanthanum (La), Cerium (Ce), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Thorium (Th), and Uranium (U) were purchased from Inorganic Ventures (Christiansburg, Virginia, USA). Working standard solution was prepared by diluting the stock standards in 2% HNO_3 and 0.5% HCl. A mixture of internal standards including bismuth (Bi), germanium (Ge), indium (In), lithium-6 (Li^6), Lu, rhodium (Rh), Sc, and terbium (Tb) purchased from Agilent Technologies (Santa Monica, CA, USA) was used for internal standard method. It was used to compensate the instrumental drift during the analysis of the REEs, Th, and U. The internal standard solution of 0.04 mg/L was on-line introduced by a mixing T piece. Two CRMs used in this study were Tomato Leaves (SRM-1573a) and Trace Elements in Spinach Leaves (SRM-1570a), (NIST, Gaithersburg, MD, USA).

Instrumentation and Analysis

Thermo Scientific^{TM} iCAP TQ triple quadrupole ICP-MS (Thermo Fisher Scientific, Waltham, Ma, USA), equipped with an ASX-560 autosampler, a MicroMist nebulizer, a quartz cyclonic spray chamber fitted with a quartz injector tube was employed for the analysis of REEs in lettuce samples. The ICP-MS operated at RF power of 1550 W was equipped with nickel sample and skimmer cones. Flow rates of Argon (99.999% purity) used as plasma and auxiliary gas were 14 L min^{-1} and 0.8 L min^{-1}, respectively. The determination of REEs, Th and U in lettuce samples was performed in triplicates using internal standard method. MARS 6 microwave digestion system (CEM, Matthews, NC, USA) was used for acid digestion prior to ICP-MS analysis.

Sample Collection and Preparation

Lettuce samples were obtained from farms and supermarkets in Thailand. The samples were washed three times with DI water to remove soil particles. The samples were freeze-dried and pulverized in a cooking blender. Then, the dried lettuce samples were kept in desiccator prior to analysis. The powdered lettuce samples (0.25 g) were weighed into 110 mL TFM vessels. The weighed samples were added with 6 mL of HNO_3 and 1 mL of H_2O_2. After 10 min pre-digestion, closed vessels were digested in a MARS^{TM} 6 microwave digestion system (CEM, NC, USA). The following digestion program was created at 15-min ramp and 30-min hold at 1000 W. After cooling down to room temperature, the digested solution was diluted with ultrapure water to a final volume of 50.00 mL and then filtered through a 0.45 µm syringe filter. Finally, REEs, Th, and U in the obtained solution of samples was analyzed using ICP-MS.

Table 1. Analytical figures of merit for the determination of REEs, Th, and U in the lettuce samples.

Element	Working range (µg/L)	Coefficient of regression, R^2	LOD (µg/L)	LOQ (µg/L)	Repeatability (%RSD)	Intermediate precision (%RSD)
La	0.001-0.25	1.0000	0.00029	0.00044	1.7	8.5
Ce	0.001-5	1.0000	0.00035	0.00058	4.5	6.2
Sm	0.01-1	1.0000	0.000089	0.000093	2.7	8.9
Eu	0.00025-0.05	0.9998	0.000064	0.00016	2.4	2.9
Gd	0.0025-0.5	1.0000	0.00011	0.00037	4.1	8.8
Th	0.001-1	1.0000	0.00050	0.00075	1.4	8.0
U	0.0005-0.25	1.0000	0.00016	0.00027	2.0	6.1

RESULTS AND DISCUSSION

Method validation for the analysis of Th, U, and REEs including La, Ce, Sm, Eu, and Gd in lettuce samples using ICP-MS is illustrated in Table 1. The evaluation of linearity was done using seven to twelve levels of standard solution. Limits of quantification (LOQs) and limits of detection (LODs) ranged from 0.000064 to 0.00054 µg/L and 0.000064 to 0.00075 µg/L, respectively. The instrumental LOD and LOQ were calculated based on the average (blank) + 3 x S_0 (blank) and average (blank) + 10 x S_0 (blank), respectively. The precisions in terms of repeatability and intermediate precisions were less than 5% and 9%, respectively.

Accuracy of the method was assessed by evaluating the recoveries of two CRMs, NIST 1573a (Tomato Leaves) and NIST 1570a (Trace Elements in Spinach Leaves). The recoveries of the studied elements in NIST 1573a and NIST 1570a were in the ranges of 79-100% and 78-96%, respectively. The results of method validation of the ICP-MS technique for the analysis of REEs, Th, and U in vegetable are shown in Table 2. The LODs of the studied elements in lettuce samples were in the range of 0.010-0.070 µg/kg. The LOQs were 0.088, 0.016, 0.019, 0.032, 0.074, 0.150, and 0.054 µg/kg for La, Ce, Sm, Eu, Gd, Th, and U, respectively.

The standard calibration plots of REEs and Th and U are presented in Figure 1 and Figure 2, respectively. Good linearity with the correlation coefficient (R^2) in the range of 0.9998 – 1.0000 was obtained for each element. In addition, the method was applied to real samples, lettuce samples. The REEs, Th, and U were determined in 20 lettuce samples obtained in Thailand, as shown in Table 3. The concentrations of La, Ce, Sm, Eu, Gd, Th, and U in lettuce samples were found in the ranges of 0.042-0.077, 0.11-0.15, 0.0116-0.0150, 0.0025-0.0042, 0.013-0.014, 0.010-0.023, and 0.0033-0.0077 mg/kg, respectively. The average concentrations of La, Ce, Sm, Eu, Gd, Th, and U were 0.061, 0.13, 0.012, 0.0033, 0.013, 0.016, and 0.0054 mg/kg, respectively. It was shown that the concentration measured by the proposed method were reliable because all concentrations found in the lettuce samples were above the LOQs for all elements. It is indicated that the proposed method has shown to be an alternative method with high potential for the analysis of all REEs (La, Ce, Sm, Eu, and Gd), Th, and U in lettuce samples. The order of average REEs, Th, and U concentrations found in lettuce samples was Eu > U> Sm > Gd > Th > La > Ce.

Table 2. Analysis of the CRMs for some REEs, Th, and U using ICP-MS.

Element	CRMs						
	NIST 1573a			NIST 1570a			LOD
	Indicative value (mg/kg)	Measured value (mg/kg)	Recovery (%)	Indicative value (mg/kg)	Measured value (mg/kg)	Recovery (%)	(µg/kg)
La	2.3	1.96	85.22	-	-	-	0.058
Ce	2	1.78	89.00	-	-	-	0.070
Sm	0.19	0.18	94.74	-	-	-	0.018
Eu	-	-	-	0.0055	0.0043	78.18	0.013
Gd	0.17	0.17	100.00	-	-	-	0.022
Th	0.12	0.095	79.17	0.0480	0.045	93.75	0.010
U	0.035	0.028	80.00	0.155	0.149	96.13	0.032

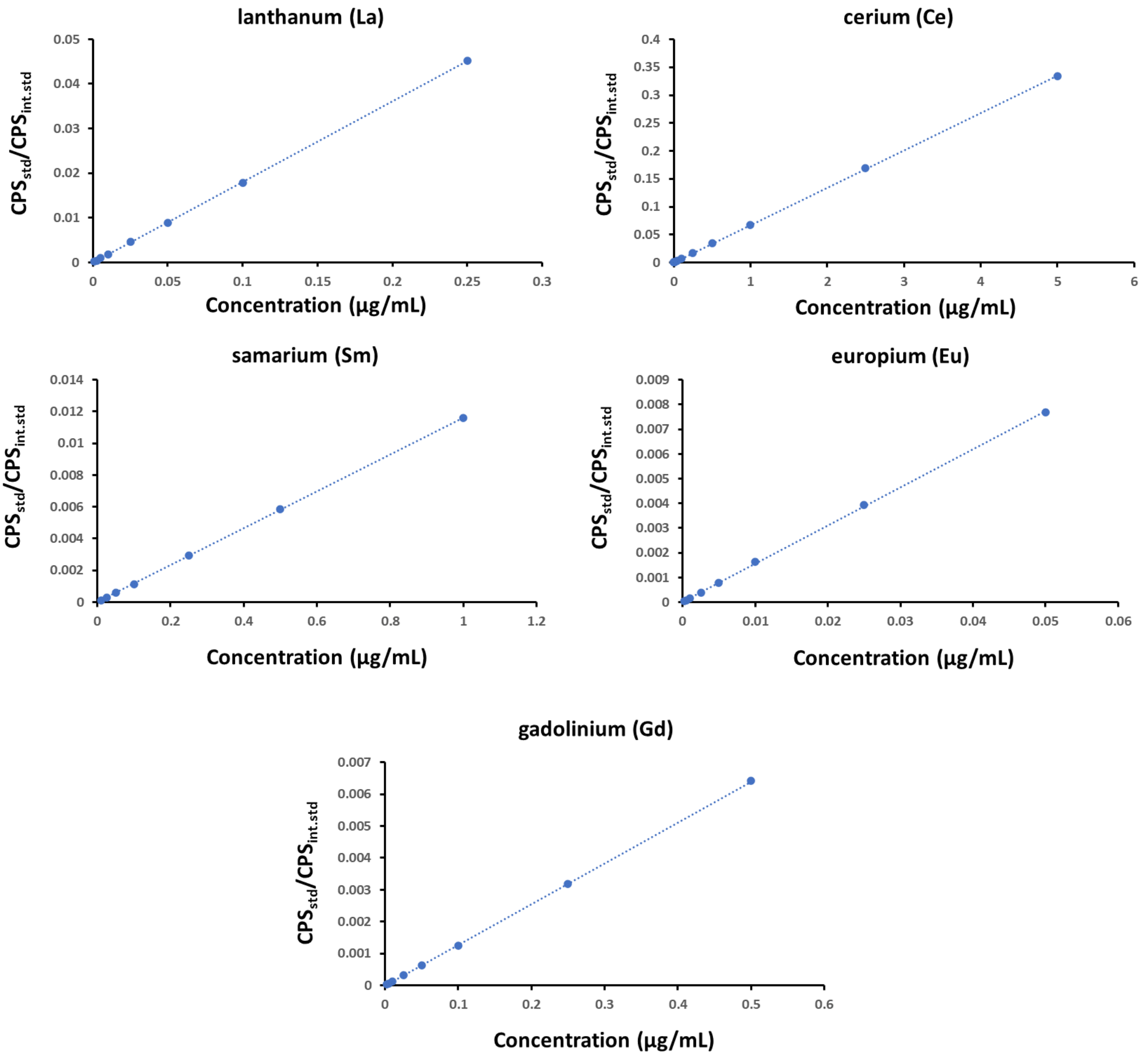

Figure 1. Calibration plots for the determination of La, Ce, Sm, Eu, and Gd in lettuce samples using ICP-MS analysis by internal standard method.

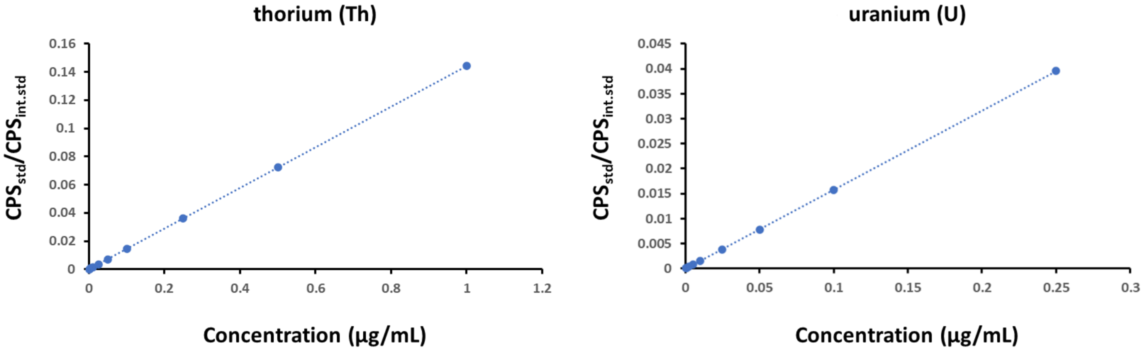

Figure 2. Calibration plots for the determination of Th and U in lettuce samples using ICP-MS analysis by internal standard method.

Table 3. Concentrations (mg/kg) ± standard deviation of REEs, Th, and U in lettuce samples measured by ICP-MS.

Sample	La	Ce	Sm	Eu	Gd	Th	U
Sample 1	0.0631±0.0058	0.124±0.00043	0.0122±0.0016	0.00342±0.00013	0.0127±0.00051	0.0123±0.000024	0.00502±0.00048
Sample 2	0.0766±0.0053	0.146±0.0079	0.0150±0.0075	0.00417±0.00015	0.0141±0.0011	0.0170±0.0019	0.00641±0.0068
Sample 3	0.0579±0.015	0.134±0.0094	0.0120±0.0043	0.00354±0.00010	0.0128±0.00080	0.0127±0.0011	0.0051±0.0039
Sample 4	0.0607±0.0084	0.133±0.014	0.0134±0.0012	0.00273±0.0018	0.0128±0.0011	0.0180±0.0011	0.00425±0.0035
Sample 5	0.0733±0.012	0.152±0.0015	0.0143±0.00050	0.00284±0.00020	0.0137±0.00060	0.0233±0.00040	0.00488±0.0055
Sample 6	0.0654±0.0093	0.140±0.011	0.0124±0.0025	0.00296±0.00020	0.0136±0.0011	0.0177±0.00060	0.00491±0.0025
Sample 7	0.0615±0.0074	0.125±0.039	0.0116±0.0016	0.00314±0.00010	0.0135±0.00060	0.0148±0.00030	0.00501±0.0062
Sample 8	0.0717±0.0030	0.142±0.00080	0.0138±0.0016	0.00354±0.00022	0.0139±0.0010	0.0194±0.0010	0.00759±0.00040
Sample 9	0.0735±0.014	0.141±0.0091	0.0136±0.0023	0.00356±0.00020	0.0135±0.0010	0.0214±0.00020	0.00773±0.0019
Sample 10	0.0723±0.018	0.130±0.0016	0.0118±0.0065	0.00348±0.00010	0.0137±0.00070	0.0203±0.00090	0.00698±0.0059
Sample 11	0.0603±0.019	0.132±0.0076	0.0116±0.00037	0.00378±0.000065	0.0131±0.0011	0.0123±0.0063	0.00537±0.00038
Sample 12	0.0621±0.0075	0.138±0.0095	0.0119±0.00050	0.00390±0.00020	0.0135±0.00060	0.0100±0.0010	0.00479±0.0047
Sample 13	0.0626±0.014	0.140±0.0027	0.0120±0.0021	0.00388±0.00010	0.0127±0.00080	0.0153±0.00080	0.00465±0.0014
Sample 14	0.0424±0.013	0.105±0.013	0.0146±0.00080	0.00245±0.00020	0.0139±0.0010	0.0105±0.00090	0.00328±0.00070
Sample 15	0.0605±0.018	0.146±0.0044	0.0132±0.0020	0.00341±0.00010	0.0134±0.00090	0.0148±0.0010	0.00498±0.0066
Sample 16	0.0509±0.0084	0.146±0.0094	0.0125±0.0053	0.00351±0.00010	0.014±0.0010	0.0103±0.00080	0.00389±0.0049
Sample 17	0.0495±0.0089	0.129±0.011	0.0136±0.0011	0.00337±0.00010	0.014±0.00080	0.0232±0.00010	0.00618±0.0038
Sample 18	0.0631±0.0095	0.111±0.0061	0.0148±0.0019	0.00262±0.00010	0.0127±0.0011	0.0166±0.00080	0.00583±0.0011
Sample 19	0.0476±0.0069	0.15±0.0096	0.0126±0.0066	0.00306±0.00020	0.0127±0.0011	0.0134±0.00010	0.00565±0.0012
Sample 20	0.0491±0.0055	0.129±0.011	0.0125±0.0053	0.00279±0.00010	0.0131±0.00090	0.0104±0.00050	0.00558±0.0048

CONCLUSION

The proposed method gave linear calibrations in the range of 0.00025–5 μg/L with correlation coefficients between 0.9998 and 1.0000. Limits of detection (LODs) and limits of quantitation (LOQs) were in the ranges of 0.000064–0.00050 μg/L and 0.000093-0.00075 μg/L, respectively. Using the proposed closed vessel method and ICP-MS, the recoveries for the analysis of the studied elements were in the ranges of 79-100% (evaluated in NIST 1573a) and 78-96% (evaluated in NIST 1570a). The proposed ICP-MS with the microwave digestion has shown to be of high potential for the analysis of some REEs (La, Ce, Sm, Eu, and Gd), Th, and U lettuce samples. La, Ce, Sm, Eu, Gd, Th, and U concentrations found in the lettuce samples were in the ranges of 0.042-0.077, 0.11-0.15, 0.0116-0.0150, 0.0025-0.0042, 0.013-0.014, 0.010-0.023, and 0.0033-0.0077 mg/kg, respectively. The obtained dataset can be further applicable to estimate the intake of some REEs, Th, and U via vegetables.

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