

## Analysis of Rare Earth Elements in *Sophora japonica* L by Inductively Coupled Plasma Mass Spectrometry

<sup>1,2</sup> QIANG SHI

<sup>1</sup>Pharmaceutical Research and Development Centre, Dezhou University, University West Road 566, Dezhou 253023, P. R. China

<sup>2</sup>Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong (Dezhou University), Dezhou 253023, P. R. China  
xinshandong2008@163.com

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**Summary:** A method for the determination of 15 Rare earth elements (REEs) in *Sophora japonica* L by inductively coupled plasma mass spectrometry (ICP-MS) was developed. The polyatomic interferences were investigated. Appropriate selection of the detection isotopes made it possible to avoid some interferences. Due to the low availability of most REEs in biological samples, most of the interferences were negligible and only interferences of  $^{135}\text{Ba}^{16}\text{O}^+$  with  $^{151}\text{Eu}^+$ ,  $^{141}\text{Pr}^{16}\text{O}^+$  with  $^{157}\text{Gd}$  and  $^{143}\text{Nd}^{16}\text{O}^+$  with  $^{159}\text{Tb}^+$  were corrected. Interferences correction was validated by comparing Eu, Gd and Tb contents in GBW 07605 tea standard reference material with and without interference subtraction. The method was applied to the analysis of REEs in flower buds, flowers, leaves, branches and ripe fruits of *Sophora japonica* L and the distribution of REEs in *Sophora japonica* L was explored. The results showed large differences in the amounts of different REEs in the same sample. It was found that the concentration of Ce was the highest and that of Lu was the lowest. The REEs contents of *Sophora japonica* L was found to generally vary in the order ripe fruits < branches < flower buds < flower < leaves, providing valuable data for understanding the effects of REEs on the efficacy of *Sophora japonica* L related herbal medicine as well as the toxicological and environmental effects for REEs application.

### Introduction

The application of REEs in herbal medicine has become a new area for pharmaceutical research and it has increasingly become the main means for increasing productivity, improving quality and enhancing medicinal efficacy of herbal medicine [1-3]. Qi *et al.* has reported that Rare earth elements (REEs) content is one of the main factors that affect four kinds of functions of herbal medicine [2]. The optimum concentration of some REEs can promote the growth of medicinal plants efficiently. At the same time, with the developments in rare earth elements application, more and more attention is being paid to their biological toxicity and environmental effects [4]. In a word, to determine the REEs content and to study their distribution in herbal plants is very important.

Inductively coupled plasma-mass spectrometry (ICP-MS), with the advantages of high sensitivity and low detection limits for REEs, simple spectra, wide dynamic range, capable of simultaneous multi-element determination and rapid isotope analysis, has been widely used to analyze REEs [5-15]. *Sophora japonica* L, which is also named "Japan Pagodatree", is often planted as street tree and it is also a very important medicinal plant and its whole plant can be used as herbal medicine. They can relieve heat and fire, cool the blood and stop bleeding

[16], and can be used for treatment of headache, dizziness, vascular hypertension, hemorrhoids and hematemesis. But until now, there are no reports about REEs analysis and their distribution in *Sophora japonica* L. In this paper, a method of analysis of REEs in *Sophora japonica* L by ICP-MS was developed. After investigation of the interferences in REEs analysis and method verification by analysis of GBW 07605 standard tea reference material, the REE content and their distribution in different parts of *Sophora japonica* L were explored, providing valuable data for understanding the effects of REEs on the efficacy of *Sophora japonica* L related herbal medicine as well as the toxicological and environmental effects for REEs applications.

### Results and Discussion

#### Interferences

In REEs analysis, the main interferences are the oxide and hydroxide ions of light REEs on heavy REEs and those of Ba on some light REEs [12-15]. Appropriate selection of the detection isotopes, enable the avoidance of some interferences. From literature, the interferences in this work were corrected with the following equation [15].

$$C_{Det(t)} = C_{Det(m)} - \kappa \times C_{int(m)} \quad (1)$$

$$\kappa = \frac{C_{Det(eq)}}{C_{int(m)}} \quad (2)$$

Where k is the interference coefficient,  $C_{Det(t)}$  is the real concentration of the element to be determined,  $C_{Det(m)}$  is the measured concentration of the element being determined,  $C_{int(m)}$  is the measured concentration of interfering element and  $C_{Det(eq)}$  is the concentration contribution from the interfering elements in the mass of the element to be determined.

A 100 ng/ml Ba and 5 ng/ml single REE solution, concentration comparable to those in the real sample were used to calculate the interfering coefficients. The interfering coefficients are shown in Table-1. After preliminary analysis with GBW 07605 tea standard reference material, it was found that the amounts of most REEs were very low and their interferences with other elements are negligible and only the interferences of  $^{135}\text{Ba}^{16}\text{O}^+$  with  $\text{Eu}^+$ ,  $^{141}\text{Pr}^{16}\text{O}^+$  with  $^{157}\text{Gd}$  and  $^{143}\text{Nd}^{16}\text{O}^+$  with  $^{159}\text{Tb}^+$  need to be corrected. To verify the efficiency of the interference correction, the interferences of  $^{135}\text{Ba}^{16}\text{O}^+$  with  $^{151}\text{Eu}^+$ ,  $^{141}\text{Pr}^{16}\text{O}^+$  with  $^{157}\text{Gd}$  and  $^{143}\text{Nd}^{16}\text{O}^+$  with  $^{159}\text{Tb}^+$  were subtracted employing the above methodology for the analysis of GBW 07605 tea standard reference material. As shown in Table-2, the corrected contents are closer to the certified values.

Table-1: The interference coefficient of oxide ions on isotopes being interfered.

Interfering ions	Interf. coef.	Interfered ions	Interfering ions	Interf. coef.	Interfered ions
$^{135}\text{Ba}^{16}\text{O}$	0.00051	$^{151}\text{Eu}$	$^{141}\text{Pr}^{16}\text{O}$	0.080	$^{157}\text{Gd}$
$^{130}\text{Ba}^{16}\text{O}$	0.000026	$^{146}\text{Nd}$	$^{143}\text{Nd}^{16}\text{O}$	0.013	$^{159}\text{Tb}$
$^{130}\text{Ba}^{16}\text{OH}$	0.000019	$^{147}\text{Sm}$	$^{150}\text{Nd}^{16}\text{O}$	0.031	$^{166}\text{Er}$
$^{147}\text{Sm}^{16}\text{O}$	0.012	$^{163}\text{Dy}$	$^{153}\text{Eu}^{16}\text{O}$	0.0053	$^{169}\text{Tm}$
$^{149}\text{Sm}^{16}\text{O}$	0.0059	$^{165}\text{Ho}$	$^{158}\text{Gd}^{16}\text{O}$	0.034	$^{174}\text{Yb}$
$^{140}\text{Ce}^{16}\text{OH}$	0.0088	$^{157}\text{Gd}$	$^{159}\text{Tb}^{16}\text{O}$	0.069	$^{175}\text{Lu}$

Table-2: Comparison of the analytical results of some analytes in GBW 07605 standard reference materials with and without subtraction of oxide interferences (n=3).

Elements	Without subtraction (µg/g)	With subtraction (µg/g)	Certified (µg/g)
Eu	0.051	0.021	0.018±0.002
Tb	0.017	0.012	0.011
Gd	0.10	0.091	0.093

### Analytical Performance

The instrumental and methodological detection limits for 15 REEs were acquired based on 3 and 10 times standard deviation [17]. The reproducibility

were based on ten consecutive determination of standard mixture. The detection limits and reproducibility were both shown in Table-3. As shown in Table-3, the RSDs for the REEs investigated ranged from 0.9% to 2.9%. The instrumental detection limits and method detection limits were in the 0.0002-0.002 ng/ml and 0.00007 to 0.0007 mg/g ranges, respectively. Certified reference material GBW07605 was analyzed to verify the accuracy of the method. As shown in Table-4, the determined results for the 15 REEs were in good agreements with the certified values.

### REEs Concentrations and Distribution

The method developed was applied to analyze REEs in flower buds, flowers, leaves, branches and ripe fruits in *Sophora japonica* L. The analytical results were shown in Table-5-7. As can be seen from Table-5 to Table-7, there are very big differences in the amounts of different REEs in the same sample with the amount of Ce the highest and that of Lu was the lowest. The concentrations of La, Ce and Nd were in the range of 0.32-1.5 µg/g, 0.42-2.3 µg/g and 0.10-1.2 µg/g, respectively. In contrast, the amounts of Tb, Tm and Lu were in the ranges 0.0011-0.028 µg/g, 0.00030-0.0090 µg/g and 0.00019-0.0079 µg/g, respectively.

In addition, by comparing the concentrations of 15 REEs in different parts of *Sophora japonica* L, it was found that there were significant differences in the amounts of the same element between samples from different parts of *Sophora japonica* L. The exception being the concentrations of Pr, Eu, Tb, Ho, Er and Tm which were higher in flower buds as compared to in the flower of *Sophora japonica* L. For a specific REE, its concentration in *Sophora japonica* L generally increases in the following order: ripe fruits, branches, flower buds, flower and leaves. Therefore the REEs levels in leaves are the highest, while those in ripe fruits are the lowest. The highest REEs contents in leaves may be due to the participation in the process of photosynthesis by REEs. The total REEs is very important for biological toxicity study, so it was investigated in detail and its values in flower buds, flower, leaves, branches and ripe fruits of *Sophora japonica* L were 2.2-2.4 µg/g, 2.8-3.3 µg/g, 5.4- 6.9 µg/g, 1.7-2.2 µg/g and 0.96-1.2 µg/g, respectively. As less than 1 kg and often less than 100 g of medicine were used in Chinese medicine practice everyday, so the daily intake of total REEs is far below 10.5 mg/d [18], its allowable daily intake limits, signifying its safety in medicinal application.

Table-3: Detection limits and reproducibility for the 15 REEs (n=10).

Elements	Detection limits of instrument (3σ, ng/ml)	Detection limits of method (10σ, μg/g)	RSD (%)	Elements	Detection limits of instrument (3σ, ng/ml)	Detection limits of method (10σ, μg/g)	RSD (%)
Y	0.001	0.0003	2.2	Tb	0.0003	0.0001	1.9
La	0.002	0.0007	1.2	Dy	0.0009	0.0003	1.8
Ce	0.002	0.0007	1.6	Ho	0.0003	0.0001	1.5
Pr	0.0004	0.0001	1.3	Er	0.0007	0.0002	2.7
Nd	0.003	0.001	2.4	Tm	0.0003	0.0001	1.6
Sm	0.002	0.0007	0.9	Yb	0.001	0.0003	2.5
Eu	0.0005	0.0002	1.4	Lu	0.0002	0.00007	1.3
Gd	0.0002	0.00007	2.1				

Table-4: REEs results of the standard reference material (GBW 07605) (n=3, μg/g).

Elements	Observed Value <sup>a</sup>	Certified Value	Elements	Observed Value	Certified Value
Y	0.37±0.01	0.36±0.03 <sup>b</sup>	Tb	0.012±0.001	0.011
La	0.58±0.03	0.60±0.03	Dy	0.077±0.004	0.074
Ce	0.95±0.04	1.0±0.1	Ho	0.023±0.002	0.019 <sup>d</sup>
Pr	0.11±0.01	0.12 <sup>c</sup>	Er	0.026±0.002	—
Nd	0.41±0.02	0.44	Tm	0.0040±0.0002	—
Sm	0.092±0.004	0.085±0.017	Yb	0.052±0.002	0.044±0.004
Eu	0.021±0.002	0.018±0.002	Lu	0.0081±0.0004	0.007
Gd	0.091±0.005	0.093			

Note: <sup>a</sup>  $\bar{x} \pm s$ , <sup>b</sup>  $\bar{x} \pm 2s / \sqrt{N}$ , s is the standard deviation, N is the number of data(≥6), the confidential level is 95%

<sup>c</sup>information value, only less than 4 data were obtained

<sup>d</sup>not available

Table-5: Contents of rare earth elements in *Sophora Japonica L* near the administrative building in the schoolyard of Dezhou University(n=3, μg/g).

Elements	Flower buds	Flower	Leaves	Branches	Ripe fruits
Y	0.17±0.01	0.24±0.01	0.69±0.02	0.16±0.01	0.036±0.002
La	0.52±0.02	0.67±0.02	1.3±0.1	0.45±0.02	0.32±0.01
Ce	0.86±0.04	1.1±0.1	2.1±0.1	0.74±0.03	0.51±0.02
Pr	0.14±0.01	0.13±0.01	0.25±0.01	0.077±0.005	0.027±0.001
Nd	0.35±0.01	0.52±0.02	1.0±0.1	0.31±0.01	0.11±0.01
Sm	0.080±0.003	0.090±0.003	0.18±0.01	0.054±0.003	0.019±0.001
Eu	0.019±0.001	0.018±0.001	0.040±0.002	0.012±0.001	0.0062±0.0003
Gd	0.056±0.002	0.082±0.005	0.17±0.01	0.050±0.003	0.017±0.001
Tb	0.011±0.001	0.0098±0.0004	0.022±0.001	0.0059±0.0002	0.0018±0.0001
Dy	0.039±0.002	0.048±0.003	0.11±0.01	0.032±0.001	0.0028±0.0001
Ho	0.093±0.004	0.088±0.005	0.021±0.001	0.0057±0.0002	0.0014±0.0001
Er	0.034±0.002	0.025±0.001	0.063±0.004	0.016±0.001	0.011±0.001
Tm	0.0081±0.0006	0.0035±0.0002	0.0083±0.0005	0.0022±0.0001	0.00036±0.00002
Yb	0.020±0.001	0.022±0.001	0.054±0.003	0.014±0.001	0.0096±0.0004
Lu	0.0024±0.0002	0.0030±0.0002	0.0080±0.0004	0.0020±0.0002	0.00036±0.00003
Total REEs	2.4±0.1	2.8±0.2	6.0±0.3	1.9±0.1	1.1±0.1

Table-6: Contents of rare earth elements in *Sophora Japonica L* near the playground in the schoolyard of Dezhou University(n=3, μg/g).

Elements	Flower buds	Flowers	Leaves	Branches	Ripe fruits
Y	0.15±0.01	0.22±0.01	0.60±0.03	0.14±0.01	0.034±0.001
La	0.46±0.02	0.61±0.03	1.1±0.1	0.39±0.02	0.31±0.01
Ce	0.75±0.03	1.0±0.1	2.0±0.1	0.68±0.03	0.42±0.02
Pr	0.11±0.01	0.10±0.01	0.22±0.02	0.067±0.004	0.026±0.002
Nd	0.39±0.02	0.48±0.02	0.90±0.03	0.26±0.01	0.10±0.01
Sm	0.071±0.003	0.084±0.003	0.15±0.01	0.049±0.002	0.018±0.001
Eu	0.022±0.002	0.019±0.001	0.040±0.003	0.012±0.001	0.0059±0.0004
Gd	0.050±0.003	0.076±0.004	0.12±0.01	0.041±0.002	0.016±0.001
Tb	0.0091±0.0007	0.010±0.001	0.019±0.001	0.0056±0.0003	0.0018±0.0001
Dy	0.028±0.001	0.049±0.002	0.070±0.003	0.028±0.001	0.0026±0.0002
Ho	0.090±0.006	0.085±0.004	0.021±0.001	0.0057±0.0002	0.0014±0.0001
Er	0.030±0.002	0.040±0.003	0.057±0.003	0.014±0.001	0.011±0.001
Tm	0.0072±0.0005	0.0029±0.0002	0.0084±0.0004	0.0019±0.0002	0.00030±0.00002
Yb	0.018±0.001	0.019±0.001	0.052±0.002	0.013±0.001	0.0092±0.0004
Lu	0.0027±0.0003	0.0041±0.0003	0.0079±0.0006	0.0019±0.0002	0.00034±0.0003
Total REEs	2.2±0.1	2.8±0.1	5.4±0.2	1.7±0.1	0.96±0.04

Table-7: Contents of rare earth elements in *Sophora Japonica L* near the new science building in the schoolyard of Dezhou University (n=3, mg/g).

Elements	Flower buds	Flowers	Leaves	Branches	Ripe fruits
Y	0.20±0.01	0.30±0.01	0.78±0.04	0.19±0.01	0.039±0.002
La	0.49±0.02	0.55±0.02	1.5±0.1	0.51±0.02	0.38±0.02
Ce	0.91±0.04	1.2±0.1	2.3±0.1	0.82±0.04	0.57±0.03
Pr	0.15±0.01	0.19±0.01	0.31±0.02	0.084±0.03	0.031±0.002
Nd	0.29±0.01	0.60±0.03	1.2±0.1	0.36±0.02	0.13±0.01
Sm	0.085±0.003	0.099±0.003	0.24±0.01	0.058±0.002	0.021±0.001
Eu	0.017±0.001	0.026±0.002	0.050±0.003	0.013±0.001	0.0062±0.0004
Gd	0.060±0.003	0.099±0.006	0.23±0.02	0.054±0.004	0.019±0.002
Tb	0.013±0.001	0.011±0.001	0.028±0.002	0.0066±0.0004	0.0011±0.0001
Dy	0.040±0.002	0.051±0.003	0.14±0.01	0.034±0.002	0.0029±0.0002
Ho	0.11±0.01	0.095±0.005	0.021±0.001	0.0061±0.0003	0.0015±0.0001
Er	0.038±0.003	0.021±0.002	0.068±0.004	0.017±0.001	0.013±0.001
Tm	0.0088±0.0004	0.0041±0.0002	0.0090±0.0004	0.0023±0.0002	0.00040±0.00004
Yb	0.023±0.001	0.027±0.001	0.054±0.003	0.014±0.001	0.010±0.001
Lu	0.0030±0.0002	0.0035±0.0002	0.0081±0.0005	0.0022±0.0002	0.0035±0.0003
Total REEs	2.4±0.1	3.3±0.2	6.9±0.3	2.2±0.1	1.2±0.1

## Experimental

### Apparatus and Conditions

The ICP-MS instrument used is a DRC-E quadruple-based instrument (PerkinElmer, USA). The ICP-MS was operated under the following conditions:

RF power = 1100 W  
 Nebulizer flow rate = 0.92 l/min  
 Auxiliary flow rate = 1.20 l/min  
 Plasma gas flow rate = 15.0 l/min  
 Sample uptake = 1.0 ml/min  
 Dwell time = 50 ms/AMU  
 Sweep times = 20.

Based on the principle of most abundance and least interference for the determined isotopes,  $^{89}\text{Y}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{146}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{151}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{172}\text{Yb}$  and  $^{175}\text{Lu}$  were selected as the detection isotopes. At the same time,  $^{135}\text{Ba}$ ,  $^{137}\text{Ba}$ ,  $^{141}\text{Pr}$  and  $^{143}\text{Nd}$  were chosen as the monitoring isotopes for interference coefficients calculation [15] and  $^{187}\text{Re}$  was chosen as the internal standard.

### Chemicals

$\text{HNO}_3$  and HF were both Metal-Oxide-Semiconductor grade (MOS) and were obtained from Beijing Chemical Reagent Research Institute (Beijing, China). HCl of supra-pure grade was provided by the Beijing Huazhun Science and Technology Development Department (Beijing, China.).  $\text{HClO}_4$  of guaranteed grade was obtained from Beijing Nan Shang Le Chemical Plant (Beijing, China). Water of 18.2 m $\Omega$ -cm was prepared using a Milli-Q water

system. 1.0 mg/ml standard solutions of each of rare earth element and barium were obtained from the National Research Center of Standard Materials (Beijing, China). Rare earth elements and barium standard solutions with appropriate concentrations used in this study were prepared by sequential dilution of the standard stock solutions with 0.32 mol/l  $\text{HNO}_3$ . GBW 07605 tea certified standard material was obtained from the State Bureau of Metrology (Beijing, China) and was used to verify the method validity.

### Sample Preparation

The samples consisting of flower buds, flowers, leaves, branches and ripe fruits were collected from three *Sophora japonica L* trees in different locations of the schoolyard of Dezhou University, Dezhou, Shandong Province, China. The first is grown near the administrative building of the Dezhou University, where there is a small forest near a lake. The second is grown in one side of the road near the playground. The third is grown in the garden near the new science building, which used to be a farmland. The flower buds, flowers, leaves, branches and ripe fruits were all from the same position in the tree and the three trees are of a similar size and age. The flower buds, flowers, leaves and branches were collected in June, 2010, while the ripe fruits were collected in later October, 2010. The samples were dried in the sun for several days after which they were ground in a mill. The samples were sieved to obtain particles of 0.25 mm in diameter. They were dried for 6 hours at 60°C before use. The moisture contents of flower buds, flowers, leaves and branches are less than 0.8% (m/m), while that of ripe fruits are less than 1.4% (m/m). Individual dried samples were weighed (0.1 g) into a 30 mL PTFE vessel. 3 ml

HNO<sub>3</sub>, 0.4 ml HClO<sub>4</sub> and 0.1ml HF were then added and the cap for the PTFE vessel was tightened. The PTFE vessel was placed in a stainless airtight vessel. The stainless vessel was heated at 170 °C in a oven for 6 h after which it was placed on a hot plate (at about 120 °C) after the cap was removed. The solution was evaporated to dryness and 0.4 ml HClO<sub>4</sub> was added. The solution was evaporated to dryness again, and the residue was dissolved in 10 ml of 0.32 mol/l HNO<sub>3</sub>.

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