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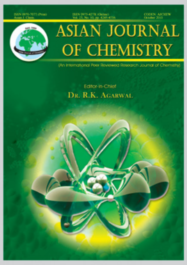

Content of Rare Earth Elements in Flos Sophorae from Different Areas

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Today more and more attention has been paid to the rare earth elements (REEs) in Chinese traditional medicine. Flos sophorae, a traditional Chinese medicinal herb, was collected from 11 areas of Dezhou and analyzed by ICP-MS to study the content and distribution of 14 kinds of rare earth elements. The results showed that ICP-MS is accurate, reliable technique for determining rare earth elements in the Chinese medicinal herbs because of its low detection limit and accuracy and the method was verified by GBW07605. The contents of total rare earth elements in flos sophorae samples from different areas ranged from 1.2077 to 2.4742 µg/g and the determined content of rare earth elements in flos sophorae varied from one area to another. The plot of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The distribution tendency of light rare earth elements (La-Gd) was relatively flat except a positive Eu anomaly, however, the distribution tendency was steep and discrepant for heavy rare earth elements (Tb-Lu). The results provided a reference for study relationship between the content of rare earth elements and curative mechanism, the pharmacology characteristics and its geology condition.

Key Words: Rare earth elements, ICP-MS, Flos sophorae.

INTRODUCTION

A long time ago, people pay attention to trace/ultra-trace rare-earth element accumulation in organism[1]. Rare earth element research in agriculture and physiology shows that rare earth element is beneficial to plant growth. Some researches showed that rare earth elements could increase yield, improve the contents of active components and agricultural product quality[2-10]. Flos sophorae is the dried flower of leguminous plant *Sophora japonica* L., which is being recorded in China pharmacopoeia[11]. Flos sophorae belongs to the legume plants and is an important medicinal origin plant, which is well known to have pharmacological activities and health care functions. In traditional medicine, flos sophorae is able to remove heat from the blood to stop blooding, with effects of cleaning the liver and discharging fire. Some researches showed that contents of rare earth elements is one of main factor that affects four kinds of functions in traditional Chinese medicine[12]. Nevertheless, no reports on rare-earth elements in flos sophorae have been published. In this study, 14 kinds of rare earth elements in flos sophorae derived from 11 county of Dezhou were measured by ICP-MS separately. The content of rare earth elements and distribution tendency were studied, providing basic data for curative mechanism and pharmacology characteristics of traditional Chinese medicinal herbs.

EXPERIMENTAL

ICP-MS (DRC-E, Perkin Elmer, USA) was operated under the following conditions: RF power: 1100 W, nebulizer flow rate of 0.92 L/min, auxiliary flow rate of 1.20 L/min, plasma gas flow rate of 15.0 L/min, sample uptake of 1.0 mL/min, dwell time of 50 ms/AMU, scan times of 20/s, integral time of 1000 ms. The analysis was performed according to the Perkin Elmer manual. The following isotopes were measured: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu.

HNO_3 (MOS, Beijing Chemical Reagent Research Institute); HCl (A.R., Shanghai Zhen Xing second chemical industry factory); HF (MOS, Beijing chemical reagent research institute); $HClO_4$ (G.R., Beijing Nan Shang Le Chemical Plant and 1.0 mg/mL standard solution of rare earth element (National research center of standards material).18.2 MΩ high-purity water provided by Milli-Q. GBW 07605 Tea leaves (State Bureau of Metrology, Beijing, China) was used to evaluate accuracy.

Preparation of samples: Flos sophorae samples were collected from 11 different areas in Dezhou. The samples were ground in mill and sieved to obtain particles 0.25 mm in diameter. They were dried for 6 h at 60 ºC before use.

0.1 g dried samples were weighed accurately and were soaked with 3 mL HNO_3 for 12 h and acid was removed with 0.4 mL $HClO_4$ and the samples were adjusted to 10 mL with 0.32 mol/L HNO_3 for measurements.

RESULTS AND DISCUSSION

Detection limits and accuracy: The detection limits for 14 rare earth elements ranged from 0.00009 to 0.005 (Table-1) and the relative standard deviation (RSD) was less than 2 %. The detection limits and RSD in Table-1 were acceptable. Standard material GBW07605 was analyzed and analytical results of rare earth elements were listed. As shown in Table- 2, the measured value accorded with standard value and the experimental method was accurate, reliable.

TABLE-1
DETECTION LIMITS AND RSD (n = 10)

Element	Detection limit (ng/mL)	RSD (%)	Element	Detection limit (ng/mL)	RSD (%)
La	0.002	0.9	Tb	0.0002	0.7
Ce	0.003	1.0	Dy	0.0002	1.5
Pr	0.001	1.3	Ho	0.0003	1.6
Nd	0.002	1.9	Er	0.0004	1.1
Sm	0.001	1.5	Tm	0.00009	0.8
Eu	0.0006	1.2	Yb	0.002	1.9
Gd	0.005	0.9	Lu	0.00009	2.0

TABLE-2
ANALYTICAL RESULTS OF RARE EARTH ELEMENTS IN GBW07605 (n = 3)

Element	Measured value (μg/g ± SD)	Standard value (μg/g ± SD)
La	0.60 ± 0.02	0.60 ± 0.04
Ce	1.02 ± 0.1	1.0 ± 0.2
Pr	0.11 ± 0.1	0.12*
Nd	0.46 ± 0.02	0.44*
Sm	0.091 ± 0.005	0.085 ± 0.023
Eu	0.019 ± 0.001	0.018 ± 0.002
Gd	0.090 ± 0.002	0.093*
Tb	0.010 ± 0.001	0.011*
Dy	0.072 ± 0.002	0.074*
Ho	0.017 ± 0.001	0.019*
Er	0.039 ± 0.002	-
Tm	0.006 ± 0.001	-
Yb	0.041 ± 0.003	0.044 ± 0.005
Lu	0.0063 ± 0.0003	0.007*

—. not available, *. referenced value

Content and distribution of rare earth elements: The results of the analyses of flos sophorae samples were summarized in Fig. 1. The contents of total rare earth elements in flos sophorae samples from different areas ranged from 1.2077 μg/g (Laoling, as dry weight, the same below) to 2.4742 μg/g (Dechengqv). As can be seen from Table-3, the contents of La, Ce and Nd were higher than 0.2 μg/g except Nd in flos sophorae from Wucheng and Pingyuan, which was the same with the results[13-15] and could be the mechanism of curative effect. In contrast, the contents of Tb, Tm and Lu were lower and content was 0.0058-0.0116, 0.0003-0.0044 and 0.0135-0.0189 μg/g, respectively. It would be seen that different rare earth elements in flos sophorae had big differences in content and the content of Ce was maximal and the content of Tm was lowest. By comparing the contents of 14 rare earth elements in flos sophorae, we found that there were highly significant differences in the contents of an element between flos sophorae sample from one area to another. For example, the content of Ce in flos sophorae from Dechengqv was 1.415 μg/g, while that from Laoling was 0.400 μg/g. However, no significant differences among Eu, Yb, Lu element. Furthermore, some elements had the same content, which could be seen from the contents of Tm in the samples from Dechengqv and Qingyun. The results showed that the contents of rare earth elements in flos sophorae from different areas were related to its geology condition and natural environment. This conclusion was confirmed by other studies on traditional Chinese medicinal herbs[13-15].

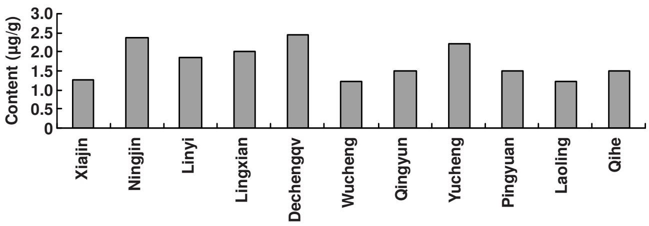

Fig. 1. Contents of rare earth elements in flos sophorae samples from different areas

Distribution tendency of rare earth elements: As can be seen from Table-3, the distribution tendency of rare earth elements was identical with Odd Harkin's rule, which coincided with other results[16,17]. In order to illuminate more clearly the distribution tendency of the rare earth elements in flos sophorae from different areas, we normalized the element concentrations (Table-4). The normalized element concentration (NEC) *versus*

TABLE-3
CONTENTS OF RARE EARTH ELEMENTS IN FLOS SOPHORAE FROM DIFFERENT AREAS (μg/g)

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Xiajin	0.238	0.441	0.0746	0.202	0.0563	0.0453	0.0475	0.0067	0.0375	0.0299	0.0581	0.0005	0.0363	0.0143
Ningjin	0.455	0.905	0.122	0.390	0.096	0.0502	0.0849	0.0116	0.0623	0.0351	0.0706	0.0006	0.0482	0.0162
Linyi	0.343	0.759	0.0961	0.285	0.0722	0.0459	0.0642	0.0088	0.0475	0.0318	0.0488	0.0020	0.0402	0.0148
Lingxian	0.263	1.0089	0.0790	0.248	0.0623	0.0450	0.0557	0.0072	0.0392	0.0301	0.111	0.0005	0.0366	0.0145
Dechengqv	0.272	1.415	0.0765	0.260	0.0621	0.0437	0.0633	0.0076	0.0422	0.0308	0.147	0.0008	0.0383	0.0149
Wucheng	0.208	0.444	0.0680	0.177	0.0570	0.0403	0.0489	0.0069	0.0389	0.0309	0.0577	0.0007	0.0386	0.0146
Qingyun	0.266	0.563	0.0795	0.202	0.0615	0.0433	0.0546	0.0077	0.0423	0.0308	0.0610	0.0008	0.0388	0.0148
Yucheng	0.458	0.809	0.123	0.395	0.0920	0.0497	0.0801	0.0111	0.0592	0.0339	0.0618	0.0003	0.0454	0.0156
Pingyuan	0.327	0.568	0.0737	0.176	0.0562	0.0510	0.0481	0.0090	0.0455	0.0321	0.0569	0.0044	0.0372	0.0135
Laoling	0.213	0.400	0.0669	0.228	0.0504	0.0441	0.0413	0.0058	0.0323	0.0288	0.0489	0.0009	0.0335	0.0138
Qihe	0.276	0.599	0.0641	0.241	0.0508	0.0423	0.0435	0.0088	0.0357	0.0318	0.0447	0.0044	0.0363	0.0189

TABLE-4
NORMALIZED RARE EARTH ELEMENTS CONCENTRATIONS

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Xiajin	0.6296	0.4518	0.5406	0.2821	0.2448	0.5231	0.1527	0.1180	0.0962	0.3445	0.2278	0.0125	0.1458	0.3695
Ningjin	1.2037	0.9273	0.8841	0.5447	0.4174	0.5797	0.2730	0.2042	0.1597	0.4044	0.2769	0.0150	0.1936	0.4186
Linyi	0.9074	0.7777	0.6964	0.3980	0.3139	0.5300	0.2064	0.1549	0.1218	0.3664	0.1914	0.0501	0.1614	0.3824
Lingxian	0.6958	1.0337	0.5725	0.3464	0.2709	0.5196	0.1791	0.1268	0.1005	0.3468	0.4353	0.0125	0.1470	0.3747
Dechengqv	0.7196	1.4498	0.5543	0.3631	0.2700	0.5046	0.2035	0.1338	0.1082	0.3548	0.5765	0.0201	0.1538	0.3850
Wucheng	0.5503	0.4549	0.4928	0.2472	0.2478	0.4654	0.1572	0.1215	0.0997	0.3560	0.2263	0.0175	0.1550	0.3773
Qingyun	0.7037	0.5768	0.5761	0.2821	0.2674	0.5000	0.1756	0.1356	0.1085	0.3548	0.2392	0.0201	0.1558	0.3824
Yucheng	1.2116	0.8289	0.8913	0.5517	0.4000	0.5739	0.2576	0.1954	0.1518	0.3906	0.2424	0.0075	0.1823	0.4031
Pingyuan	0.8651	0.5820	0.5341	0.2458	0.2443	0.5889	0.1547	0.1585	0.1167	0.3698	0.2231	0.1103	0.1494	0.3488
Laoling	0.5635	0.4098	0.4848	0.3184	0.2191	0.5092	0.1328	0.1021	0.0828	0.3318	0.1918	0.0226	0.1345	0.3566
Qihe	0.7302	0.6137	0.4645	0.3366	0.2209	0.4885	0.1399	0.1549	0.0915	0.3664	0.1753	0.1103	0.1458	0.4884

atomic number was plotted for clarity (Fig. 2). The plot of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The distribution tendency of light rare earth elements (La-Gd) was relatively flat except a positive Eu anomaly, however, the distribution tendency was steep and discrepant for heavy rare earth elements (Tb-Lu)[18]. The phenomenon suggests that rare earth elements in plant has an interdependent relationship. On the other hand, discrepancy of heavy rare earth elements may be related to existing state of element. Furthermore, the results provide a reference for study on relationship between the contents of rare earth elements and curative mechanism, the pharmacological characteristics and its geology condition.

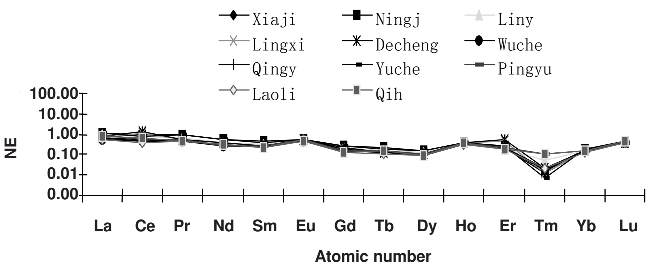

Fig. 2. Distribution tendency of concentrations of rare earth elements after normalization

Conclusion

ICP-MS is a reliable technique for determining rare earth elements in the Chinese medicinal herbs because of its low detection limit and accuracy. The content of rare earth elements in flos sophorae varies largely with the samples collected from one area to another, indicating that it is influenced by an environment factor. The plot of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The distribution tendency of light rare earth elements (La-Gd) was relatively flat except a positive Eu anomaly, however, the distribution tendency was steep and discrepant for heavy rare earth elements (Tb-Lu). The phenomenon suggests that rare earth elements in plant has an interdependent relationship. On the other hand, discrepancy of heavy rare earth elements may be related to existing state of element. Furthermore, the results provide a reference for study on relationship between the contents of rare earth elements and curative mechanism, the pharmacologic characteristics and its geology condition.

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