ORIGINAL ARTICLES

Determination of wholesome elements and heavy metals in safflower (*Carthamus tinctorius L.*) from Xinjiang and Henan by ICP-MS/ICP-AES

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Abstract: An inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) was developed to determine 19 elements in safflower, a traditional Chinese medicinal herb from Xinjiang Autonomous Region and Henan Province of China. Totally 19 elements in safflower included heavy metals, i.e. As, Cd, Cu, Hg and Pb, and wholesome elements, i.e. Al, Ca, Co, Cr, Fe, Mg, Mn, Mo, Ni, P, Se, Sr, V and Zn. The results showed that the concentrations of heavy metals in safflower samples were both low, all of which met the national hygiene standards except for Pb in Xinjiang sample. Meanwhile, the distribution tendency of elements in the two samples was similar, which indicated that the plant might absorb given elements in a proportional way. The method can be used for the quality control of elements in safflower, and it provides a way for the determination of the contents of safflower from Xinjiang and Henan.

Keywords: inductively coupled plasma mass spectrometry; inductively coupled plasma atomic emission spectrometry; wholesome elements; heavy metals; safflower

1 Introduction

The use of herbal medicine, also called traditional Chinese medicine (TCM) in China, is very common in the Oriental culture. This form of complementary and alternative medicine has been around for more than 3000 years. In the Chinese culture, many medicinal materials and health products were used. For example, safflower (*Carthamus tinctorius L.*) is an annual, broad leaf oil seed and medicinal crop which belongs to the family Compositae [1]. It is widely cultivated in agricultural production system of Asia, Europe, Australia and the America as a source of high-quality vegetable and industrial oil [2]. It has long been used as a food colorant, dye, and herbal medicine in Oriental countries [3]. Safflower edible oil cultivars have the highest quantity of polyunsaturated fatty acids. It is also used as a feed for livestock [4]. Safflower seeds have long been clinically used in Korea as herbal medicine to promote bone formation and prevent osteoporosis. There are some reports about anti-oxidative compounds from safflower describing their activity in scavenging free radical species [5]. It is also reported that the major antioxidants in safflower seed, serotonin derivatives, may inhibit low-density lipoprotein (LDL) oxidation and atherosclerosis in apolipoprotein E-deficient mice [6-10].

Because of the increasing interest in traditional Chinese medicinal products such as safflower, it is important to determine whether they are safe for consumption. Levels of toxic elements such as As, Cu, Cd, Hg and Pb in the plant samples must be determined. The levels of toxic elements are usually at the μg/mL level, thus necessitating the use of ICP-MS for their determination [11, 12]. ICP-MS offers the advantages of high sensitivity and simultaneous multi-element analysis capability. Furthermore, some common elements such as K, Na and P are essential for health and the quantification of these elements is important for nutritional purposes. Since the concentrations of these elements are usually at the percentage level, the use of ICP-AES is an appropriate choice for their determination because no further dilution of the sample solution is needed [13,14].

In this work, the capability of ICP-MS/ICP-AES for the quantification of the levels of heavy metals and wholesome elements in safflower was evaluated. ICP-MS was used to determine several heavy metals and lower levels of elements, i.e. As, Cd, Cu, Hg, Pb, Al, Co, Cr, Mn, Mo, Ni, Se, V, and Zn, while ICP-AES was used to measure the higher concentration of elements, i.e. Ca, Fe, Mg, P, and Sr. This method was then applied to the analysis of safflower from Xinjiang Autonomous Region and Henan Province. And the differences between region and content of elements were also investigated, thereby providing basis for typical analysis of elements and offering a way to study the relationship between the elements and the actions of TCM.

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2 Experimental

2.1 Materials and reagents

HNO_3 (BV-Ⅲ) was purchased from Beijing Institute of Chemical Reagents. $HClO_4$ was obtained from G. R. Tianjin Eastern Chemical Plant. Ultra-pure water with conductivity of 5.5×10^{-6} S/m was measured on conductometer model DOS-11A(Shuangfeng Equipment Factory, Beijing). Mixed standard solution was prepared by diluting 1000 μg/mL standard solution of different elements. Stock buffer was purchased from the National Research Center for Certified Reference Material.

2.2 Instrumentation

The analysis was made on Perkin-Elmer Sciex Elan 5000 ICP-MS and ICP-AES (Beijing Kechuang Haiguang Instrument Company). Type 800 centrifuge was from Shanghai Operation Instrument Company, and 50 W ultrasonicator was from Peking University Apparatus Factory.

2.3 Preparation of samples

Safflower was from two different regions including No. 1 Xinjiang and No. 2 Henan. The samples were ground and sieved to obtain particles less than 0.25 mm in diameter. They were dried for 6 h at 60 ℃ before use. About 0.20 g dried samples were weighed and digested with 5 mL HNO_3 and $HClO_4$ (20 : 1, v/v). After complete digestion and removal of acid, the samples were adjusted to 5 mL with pure water, ready for measurement.

Sample solution was measured by ICP-MS/ICP-AES. The parameters for ICP-MS were forward power 1000 W, nebulizer gas flow rate 0.8 L/min, and sampling depth 10 mm; the parameters for ICP-AES were forward power 1150 W, nebulizer pressure 0.5 psi, flow capacity of auxiliary gas 1.0 L/min, and lifting capacity of pump 1.2 mL/min.

3 Results and discussion

3.1 Linearity, detection limits and accuracy

To determine the linearity of the response versus concentration for the elements, a series of mixed standard solutions at the concentrations from 0.00755 to 99.98 ng/mL(ICP-MS) and 0.05 to 5 μg/mL (ICP-AES) were tested, respectively. The results of regression analysis on calibration curves are presented in Tables 1 and 2. As can be seen, for all the analyzed elements, the correlation coefficient of the calibration curves was no less than 0.9938.

The detection limits for the 19 elements by ICP-MS and ICP-AES methods ranged from 0.001 to 20.8 ng/mL (Tables 3 and 4). The accuracy of both the ICP-MS and ICP-AES methods was evaluated by calibrating both instruments with a blank and the standards. The accuracy range was defined as the concentration for which the results (in concentration units) were within ± 10% of the true value (designated value). The results are listed in Tables 3 and 4 for the ICP-MS and ICP-AES, respectively. As shown in Tables 3 and 4, the recoveries for most elements were between 90% and 110%, and the relative standard deviations (RSDs) were less than 5.25% for most of the samples. The recoveries and RSDs listed were acceptable.

Table 1 Results of regression analysis on calibration curves by ICP-MS

Element	Regression equation	Correlation coefficient	Linear range (ng/mL)
As	$y = 0.6117x - 0.0206$	0.9994	0.50 - 10.14
Cd	$y = 0.564x + 0.104$	0.9974	0.10 - 9.73
Cu	$y = 0.3951x + 0.005$	0.9994	0.10 - 19.97
Hg	$y = 1.5918x - 0.0086$	0.9938	0.00755 - 0.21000
Pb	$y = 4.6763x + 0.9911$	0.9962	0.10 - 9.67
Al	$y = 3.06x + 0.4275$	0.9967	0.50 - 10.60
Co	$y = 4.4889x + 0.9861$	0.9955	0.10 - 9.64
Cr	$y = 2.2035x + 0.0766$	0.9998	0.10 - 9.97
Mn	$y = 3.2389x + 0.2565$	0.9997	0.10 - 9.91
Mo	$y = 0.8166x + 0.1544$	0.9969	0.10 - 9.70
Ni	$y = 0.9929x + 0.1884$	0.9968	0.10 - 9.69
Se	$y = 0.068x - 0.0048$	0.9985	0.50 - 10.23
V	$y = 0.1078x - 0.0006$	0.9992	0.10 - 10.13
Zn	$y = 0.0994x - 0.0061$	0.9996	0.10 - 99.98

Table 2 Results of regression analysis on calibration curves by ICP-AES

Element	Regression equation	Correlation coefficient	Linear range (μg/mL)
Ca	$y = 2947.8x + 0.9335$	0.9995	0.1 - 5.0
Fe	$y = 3485.8x + 18.943$	0.9998	0.1 - 5.0
Mg	$y = 99539x + 465.25$	0.9997	0.1 - 5.0
P	$y = 324x - 1.8124$	0.9999	0.1 - 5.0
Sr	$y = 234342x + 653.88$	0.9996	0.05 - 2.00

Table 3 Detection limit and accuracy by ICP-MS

Element	Detection limit (ng/mL)	Recovery ($n = 5$, %)	RSD (%)
As	0.021	99.90 ± 4.37	4.37
Cd	0.003	104.70 ± 2.15	2.05
Cu	3.750	99.50 ± 2.44	2.45
Hg	0.024	94.00 ± 2.97	3.16
Pb	0.120	103.80 ± 1.66	1.60
Al	20.800	103.60 ± 5.44	5.25
Co	0.001	104.60 ± 2.33	2.23
Cr	0.002	101.60 ± 2.40	2.36
Mn	0.500	102.10 ± 0.83	0.81
Mo	0.002	103.40 ± 4.98	4.82
Ni	0.005	103.60 ± 2.36	2.28
Se	0.050	100.40 ± 5.19	5.17
V	0.002	107.50 ± 2.45	2.28
Zn	0.470	101.00 ± 2.07	2.05