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Research Article

Elemental Fingerprint of Herbal Medicines Formed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

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Abstract

Herbal medicines contain multiple compounds, each of which may be relevant to the medicine's pharmacological activity. A method referred to as 'elemental fingerprint', which is accurate and rapid, is used in this paper. It provides a more powerful approach than the single component analysis to the quality control of herbal medicines as it furnishes information on several elements and the ratios at which they are present. Eight elements, Li, Mn, Ni, Zn, Cd, Pb, Se, Cu, in 21 samples of herbal medicines were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The data analysis was performed with EXCEL and SPSS. The experimental results clearly demonstrated that the proposed method was a useful tool to control the quality of herbal medicines.

Keywords: Herbal Medicines, Elemental Fingerprint, ICP-AES

1. Introduction

Herbal medicines, which have been in the Chinese material medicines and other folk medicines for thousands of years, are being increasingly used nowadays in the whole world for improving health conditions of humans as well as for the prevention and treatment of various diseases [1]. However, as herbal medicines may contain hundreds of ingredients, our knowledge about their pharmacological activities is still limited [1]. Furthermore, the analytical methods for the quality control of herbal medicines have thus far not been standardized [2],[3]. Traditionally, according to their different morphology, the identification of herbal medicines is carried out by the experienced herbalist doctor, which prevents the spread of herbal medicines [4]. The key factor is the construction of both quality control standards for raw materials and the standardization of finished herbal drugs. Up to date, variation methods had been designed to solve aforementioned problems. For example, chromatographic fingerprint analysis, which uses modern chromatographic techniques such as gas chromatograph (GC), high-performance liquid chromatography (HPLC) or high-performance thin layer chromatography (HPTLC) to construct specific patterns of recognition for multiple compounds in herbal medicine, has been adopted to identify the quality of herbal medicines [5]. However, the current spectroscopic fingerprinting technology that aimed at specific organic components, not suitable for the complex multi-component environment. Furthermore, elemental fingerprint techniques, based on elemental composition and multivariate statistical analysis, have been used to solve this problem [5] [6]. elemental fingerprint techniques.

In this article, we further developed elemental fingerprint techniques to control the quality of herbal medicines. The contents of Li, Mn, Ni, Zn, Cd, Pb, Se, and Cu in 21 species of herbal medicines have been determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES) to establish the elemental fingerprint.

2. Experimental

2.1 Instrument

An Optima 4300DV plasma emission spectrometer (Perkin Elmer Corporation, United States) was used for the determination of analytes.MDS-10 microwave digestion system (Sineo Microwave Chemistry Technology (China) Co., LTD) was used to prepare the samples.

2.2 Reagents and materials

All reagents were of analytical-reagent grade, and distilled, deionized water was used throughout. Standard Solution: Using the standard solution provided by Perkin Elmer. We prepared the mixed standard solution according to the concentration range of each element in samples.

2.3 Preparation of samples

Samples of 21 herbal medicines that were most frequently consumed were obtained commercially from a local store of Chinese traditional medicines in Qingdao, Shandong Province, China. Each of the samples had been identified by an experienced herbalist. All the samples from the packages

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were ground into a fine powder and dried at 80 ºC for 24 h prior to use.

0.5000g sample that was accurately weighed was put into Teflon digestion tank; added 5mL concentrated HNO_3 soaking overnight. Then we added 3mL H_2O_2, digested in the microwave digestion system for 8 min until completely, transferred to 50mL volumetric flask diluted using 5% HNO_3 solution to the mark. Two parallel copies of the blank were prepared in the same way.

2.4 Determination by ICP-AES method

Booting the system into Winlab 32 operating software by Optima 4300DV plasma emission spectrometer operating procedures, establishing the analytical methods, Plasma ignited. The blank solution, standard solution and sample solution was determined in order. Instrument operating parameters are listed in Table 1 and Table 2.

Table 1. Operation Parameters of Optima 4300DV

Name	Parameters
Nebulizer pressure(KPa)	125.0
Cooling gas flow rate(L/min)	0.8
Carrier gas flow rate(L/min)	15
Auxiliary gas flow rate(L/min)	0.2
Peristaltic pump flow rate(mL/min)	1.5
Nebulizer flow rate(L/min)	0.8

Table 2. Detection wavelengths(nm-1)

Li	670.784	Mn	257.610
Cd	228.802	Ni	231.604
Cu	327.393	Pb	220.353
Zn	206.200	Se	196.026

2.5 Data analysis

For the chemometric study, each of the herbal medicines samples was characterized by 8 chemical descriptors which are the contents of the analyzed elements. The software EXCEL2003 (Microsoft Corporation, USA) was applied to plot a bar graph from the data matrix composed of 8 columns (the analyzed elements) and 21 rows (herbal medicines samples). The statistical package SPSS 17.0 (SPSS Inc., USA) was used for statistical analysis.

3. Results and discussion

3.1 Elements in herbal medicines

Herbal medicines contain various elements. Some of these elements are benefit to human beings such as Mn, Cu, Zn, Se, etc., while others are non-essential to humans or even toxic elements such as Cd, Pb [7], [8]. Much research have been made to establish the normal concentration range and evaluate their role in herbal medicines [9], [10]. To construct fingerprints of herbal medicines, eight elements in 21 samples are determined. The mean concentrations of elements determined in this study are shown in Table 3. As can be seen from these values, Mn and Zn are the elements with a major content in all samples, with average concentrations of 44.6501 and 43.7744 μg/g, respectively. While other elements present lower contents, their average values are less than 5 μg/g. Several trace elements, such as Mn, Zn, Cu and Se, are chemical elements that play an important role as oligo elements in biological systems. However, these micronutrient elements may also be the origin of adverse effects on living organisms if the dosages exceed certain levels.

Table 3. Contents of elements in the herbal medicines samples, presented as means (n = 6)

Element (μg/g)	Baixianpi	Baizhi	Baihe	Dingxiang	Honghua	Huluba	Jiujie changpu
Li	0.3688	0.6000	0.4153	0.1152	1.6580	0.8201	0.4124
Mn	9.9083	15.3958	15.7309	248.6279	24.8103	20.1700	28.2400
Ni	1.9837	3.1374	3.1923	1.9944	4.0286	2.2450	0.4359
Zn	11.9617	33.9332	38.2620	25.6481	50.5094	55.8300	46.7200
Cd	1.5849	1.9646	2.6418	1.5765	1.6580	0.0968	0.1504
Pb	0.2871	0.3942	1.4881	8.6217	6.9414	1.5800	4.8710
Se	1.5230	0.2320	1.8063	1.4580	0.6694	3.3540	3.0160
Cu	3.7842	1.5109	4.2880	4.3799	9.6153	0.6055	7.6514

Element (μg/g)	Huanglian	Juemingzi	Lianzi	Ruxiang	Hujisheng	Tianma	Xiaohuixiang
Li	0.3158	0.1732	0.0098	0.1613	0.3558	0.1583	4.1400
Mn	117.9000	10.3627	44.1600	19.5000	46.5200	9.7842	24.2300
Ni	2.9260	2.5160	2.6360	0.4132	0.4245	2.1792	1.2900
Zn	156.3000	69.8100	37.4900	6.5741	9.1482	28.1913	39.7500
Cd	2.1440	1.4400	1.4851	0.1815	0.4503	1.8693	0.0000
Pb	10.4200	0.7813	0.3178	2.3660	3.6470	0.9194	3.0300
Se	2.6650	2.3630	0.4900	6.3660	2.8100	6.4599	0.6200
Cu	12.6100	9.3090	11.7740	2.3795	5.4179	0.6812	0.5711

Element (μg/g)	Yinchen	Yinxingye	Yuzhu	Pangdahai	Zisuzi	Jinqiancao	Ziyulan
Li	2.7090	3.0450	0.7053	0.0299	0.9882	2.6040	0.0499
Mn	63.1400	13.6800	32.2174	22.2554	36.5396	99.0296	35.4500
Ni	2.7560	2.3120	2.4538	1.6267	0.9882	2.0510	5.1210
Zn	25.4600	21.3200	26.8528	42.8443	30.2475	0.0000	162.4100
Cd	0.2360	1.5770	2.2253	1.6766	0.0540	0.9496	1.8966
Pb	4.7820	3.5200	1.8478	0.8583	1.6324	11.7172	0.0000
Se	0.5940	0.0000	0.6656	0.0000	2.0017	0.8671	2.6951
Cu	16.6200	4.5547	0.7513	0.8064	3.8754	7.5537	7.4266

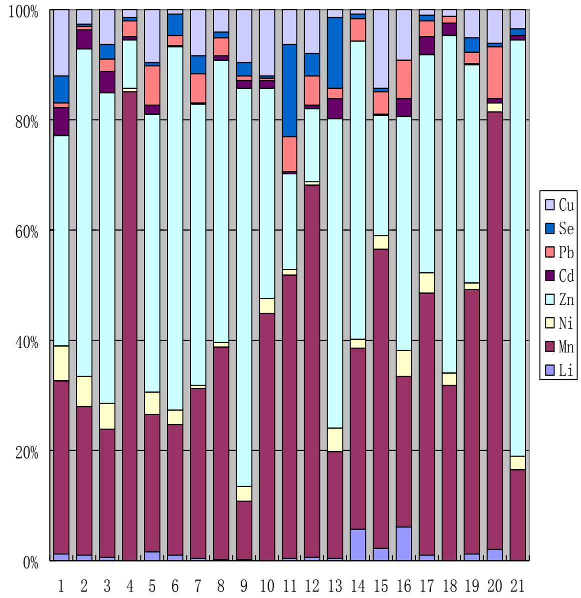

Fig 1. Elemental fingerprints of 21 herbal medicines samples.

1 = Baixianpi; 2 = Baizhi;3 = Baihe; 4 = Dingxiang; 5 = Honghua; 6 = Huluba; 7 = Jiujie changpu; 8 = Huanglian; 9 = Juemingzi; 10 = Lianzi; 11 = Ruxiang; 12 = Hujisheng; 13 = Tianma; 14 = Xiaohuixiang; 15 = Yinchen; 16 = Yinxingye; 17 = Yuzhu; 18 = Pangdahai; 19 = Zisuzi; 20 = Jinqiancao; 21 = Ziyulan.

3.2 Fingerprint analysis of herbal medicines

As mentioned above, the analysis of one or more compounds as markers fails to identify a specific herbal medicine, because the components or markers are not unique to a specific herbal medicines and an active ingredient of a certain herbal medicine can be found in many other herbs [9]. The fingerprint of herbal medicines is an identity of single herbal medicine via building a unique feature. In fact, different kind of features can be selected to represent the herbal medicines and can be used as fingerprints. In the present paper, the mean contents of eight elements have been determined in samples of herbal medicines to establish elemental fingerprint for quality control by using ICP-AES. For convenience of recognition, the data obtained from the experiment are transformed to plot a percentage-stacked graph (Fig. 1). Because the concentration and proportion of elements are different among these herbal medicines, it can be easily found that each herbal medicine is corresponding with a unique fingerprint pattern. With the help of fingerprint, we can easily evaluate the identity and quality of herbal medicines.

3.3 Evaluation of elemental fingerprint by similarity analysis

Similarity analysis is a powerful tool in establishing and evaluating the fingerprints of herbal medicines. By using similarity analysis, the similarity of herbal medicines can be evaluated by Euclidean distance (d_r), cosine similarity (C_r), and Pearson product-moment correlation coefficient (r_r) [11]. The formulas are as followed:

$$d_r = \left[\sum_{i=1}^{m}\left(X_i - Y_i\right)^2\right]^{\frac{1}{2}}$$

$$C_r = \frac{\sum_{i=1}^{m} X_i \bullet Y_i}{\sqrt{\left(\sum_{i=1}^{m} X^2{}_i\right)\left(\sum_{i=1}^{m} Y^2{}_i\right)}}$$

$$r_r = \frac{\sum_{i=1}^{m}\left(X_i - \overline{X}\right)\left(Y_i - \overline{Y}\right)}{\sqrt{\sum_{i=1}^{m}\left(X_i - \overline{X}\right)^2 \sum_{i=1}^{m}\left(Y_i - \overline{Y}\right)^2}}$$

where X_i and Y_i are ith elements in two fingerprints and m is the number of element, $\overline{X}$ and $\overline{Y}$ are the average values of elements in fingerprints.

In our study, three samples of Zisuzi were determined to evaluate the fingerprint's discriminatory power. The concentrations of elements in three samples are listed in Table 4. By using SPSS, Euclidean distance, cosine similarity, and Pearson product-moment correlation coefficient can be calculated easily. Three samples shows a high degree of similarity with Zisuzi's fingerprint, giving the values of 0.846, 1.169, and 1.467 in Euclidean distance, 1.000, 1.000, and 1.000 in cosine similarity, 1.000, 1.000, and 1.000 in Pearson product-moment correlation coefficient.

Table 4. Contents of elements in the three samples of Zisuzi, presented as means (n = 6)

Element (μg/g)	Sample 1	Sample 2	Sample 3
Li	0.9756	0.9868	0.9841
Mn	36.1753	37.6829	38.0057
Ni	0.9846	0.9753	0.9873
Zn	31.0025	30.1739	30.2753
Cd	0.0526	0.0530	0.0547
Pb	1.6078	1.6322	1.6310
Se	2.1081	2.1753	2.0173
Cu	3.9021	3.7215	3.9052

In brief, it can be seen that the herbal medicines can be effectively discriminated according to their concentration and proportion of elements. Each herbal medicine presented a distinctive elemental fingerprint, as was indicated by similarity analysis.

4. Conclusion

In this study, we developed elemental fingerprint to identify the quality of herbal medicines instead of reported chromatographic fingerprint. The results indicated that elemental fingerprint is an effective and reliable identity for the purpose of species authentication and quality control of herbal medicines. In addition, this method can be extended to the other herbal medicines, which may have wide potential applications in the identification of herbal medicines.

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