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微波消解-火焰原子吸收光谱法测定秦艽和麻花秦艽中多种微量元素

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摘 要 密封微波消解已被运用于火焰原子吸收光谱法对中草药中微量元素含量的测定过程中。微波消解法具有方便省力, 安全快捷, 污染少, 样品溶解完全等特点。选用硝酸和双氧水(5∶1)的混合消化液作为消解剂进行微波消解。运用火焰原子吸收光谱法测定了秦艽和麻花秦艽中的 Fe, Mn, Ni, Cu, Zn, Ca, Mg, Cr 等八种微量元素的含量。进行了微波消解条件的选择及消化结果精密度实验, 该方法的加标回收率为88.1%～114.5%, 相对标准偏差(RSD) < 3.12%, 具有较为良好的准确度和精密度。结果表明, 秦艽和麻花秦艽均富含 Ca, Mg, Fe, Mn, Zn 等元素, 而 Ni 和 Cr 含量均较低。通过对秦艽和麻花秦艽微量元素含量的比较, 发现秦艽中的 Mg, Fe, Mn, Ni 含量较高, 而麻花秦艽中的 Zn, Cu, Ca, Cr 含量较高。此结果为探讨微量元素与秦艽和麻花秦艽的药效关系提供了一定的科学数据。并且, 通过本实验为秦艽和麻花秦艽的进一步研究和综合开发利用提供了新的科学依据。

关键词 微波消解; 火焰原子吸收光谱法; 秦艽; 麻花秦艽; 微量元素

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引 言

秦艽为龙胆科植物秦艽(*Gentiana macrophlla Pall.*)的干燥根。麻花秦艽为龙胆科植物麻花秦艽(*Gentiana straminea Maxim.*)的干燥根。两者为同科同属的不同种植物, 2005版中国药典一部将两者均列为中药秦艽药材来源品种。中药秦艽为临床常用中药, 又名西秦艽、大秦艽、左秦艽、左扭根[1]等, 具有祛风湿, 清虚热, 止痹痛的功效[2], 主要用于治疗风湿痹痛、筋骨拘挛、便血、骨蒸潮热小儿疳热、小便不利等[3]。

现代科学研究已证明特定状态的微量元素是维持健康和防病治病的必要条件之一, 微量元素是中药归经和药性物质基础的重要组成部分[4]。长期以来, 人们对中药的有效成分研究偏重于其有机成分, 随着对中药成分的深入探讨, 无机成分尤其是微量元素日益被人们所重视[5-7]。目前, 相关报道对秦艽有机成分、药理研究及有效成分含量测定研究较多[8-10], 但对其微量元素研究未见报道。微波消解技术是一种较新的试样消解技术, 其具有快速、准确、省试剂、省费用、污染少等特点[11]。本文运用微波消解-火焰原子吸收法对两种中国药典规定的中药秦艽药用品种的 Fe, Mn, Ni, Cu, Zn, Ca, Mg, Cr 等八种微量元素含量进行了测定, 并将二者的含量进行了比较, 为探讨二者微量元素与质量及药效关系提供了一定的科学依据。

1 实验部分

1.1 仪器及工作条件

220FS原子吸收分光光度计(美国瓦里安公司)。ETHOS D高压微波消解装置(意大利 Milestone 公司)。工作条件见表1。

1.2 试剂和溶液

HNO_3 优级纯, H_2O_2 分析纯, 测定和分析用水均为去离子水。待测元素标准使用液(浓度均为1 000 μg·mL^{-1})由中国标准物质研究所提供。

1.3 样品来源及处理

秦艽采自甘肃天水小陇山,麻花秦艽由汪荣斌采自甘肃甘南扎油沟, 经本院生药学专业张西玲教授鉴定。样品用自来水冲洗数次后, 用去离子水洗涤3次, 过滤、晾干放入烘箱中, 温度控制在60 ℃, 保持8 h, 待干燥后取出, 分别粉碎后用研钵研细, 过100目筛。准确称取秦艽和麻花艽样品粉末各0.500 0 g于干净的聚四氟乙烯消解罐中, 加入消解

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剂 10 mL HNO_3 和 2 mL H_2O_2，盖上聚四氟乙烯盖子，放置过夜。次日选适当的温度和时间进行消解，冷却后将消解液转移至 25 mL 容量瓶中，用去离子水稀释溶液至刻度待测。同时做样品空白。

Table 1　Operating conditions

元素	波长 / nm	灯电流 / mA	狭缝 / nm	乙炔流量 / (L·min⁻¹)	空气流量 / (L·min⁻¹)
Ni	232.0	4.0	0.2	2.00	13.50
Zn	213.9	5.0	1.0	2.00	13.50
Fe	248.3	5.0	2.0	2.00	13.50
Mn	279.5	5.0	2.0	2.00	13.50
Cu	324.8	4.0	0.5	2.00	13.50
Cr	357.9	5.0	0.2	2.00	13.50
Ca	422.7	10.0	0.5	2.00	13.50
Mg	285.2	4.0	0.5	2.00	13.50

1.4　标准曲线

分别吸取适量的标准使用液，用去离子水稀释成表 2 的系列标准溶液。

Table 2　Standard solution(μg·mL⁻¹)

元素	Ni	Zn	Fe	Mn	Cu	Cr	Ca	Mg
标准 1	0	0	0	0	0	0	0	0
标准 2	0.02	0.1	0.1	1.0	0.1	0.1	1.0	1.0
标准 3	0.04	0.2	0.2	2.0	0.2	0.2	2.0	2.0
标准 4	0.06	0.3	0.3	3.0	0.3	0.3	3.0	3.0
标准 5	0.08	0.4	0.4	4.0	0.4	0.4	4.0	4.0
标准 6	0.10	0.5	0.5	5.0	0.5	0.5	5.0	5.0

1.5　元素分析

采用火焰原子吸收法测定样品中各元素含量。根据元素含量及测定元素灵敏度的不同，测定各元素时分别稀释适当的倍数。

2　结果与讨论

2.1　测定结果

测定结果见表 3。

Table 3　Contents of trace elements in samples(n = 4)

元素	秦艽		麻花艽	
	平均值/ (μg·g⁻¹)	RSD/ %	平均值/ (μg·g⁻¹)	RSD/ %
Ni	3.01	0.42	1.23	3.12
Zn	33.28	1.24	49.79	1.47
Fe	196.07	1.86	141.11	1.89
Mn	154.32	2.07	143.23	0.02
Cu	50.65	0.63	80.33	0.42
Cr	3.85	1.76	4.48	2.86
Ca	3 665.14	0.46	4 574.76	2.07
Mg	1 028.86	1.53	798.73	1.33

2.2　消解条件的选择

中草药的样品消解[12-14]常用硝酸、盐酸、硫酸、磷酸、高氯酸、氢氟酸、过氧化氢等作为溶剂[15]。通过大量的实验工作表明，选用硝酸和双氧水(5∶1)混合的消化液，并通过控制适当的温度(120～180 ℃)及时间(5～15 min)可完全消解样品。微波消解技术加速了样品的分解，改进了传统的消化模式，改善了工作环境以及减轻了分析人员的劳动强度。

2.3　分析线的选择

根据检出限低、灵敏度高、共存元素谱线干扰少、光谱干扰程度低的原则选择以下分析线(nm)进行分析：Ni 232.0，Zn 213.9，Fe 248.3，Mn 279.5，Cu 324.8，Cr 357.9，Ca 422.7，Mg 285.2。

2.4　回收率和精密度实验

为了考察方法的可靠性，对实验结果进行了回收率和精密度的考察，结果见表 4。

Table 4　RSD and recovery of the method(n = 5)

元素	秦艽		麻花艽	
	回收率/ %	RSD/ %	回收率/ %	RSD/ %
Ni	114.5	3.41	110.3	2.54
Zn	103.8	2.12	103.6	1.69
Fe	106.7	1.74	100.5	2.03
Mn	98.1	0.83	97.0	1.23
Cu	90.5	1.58	105.6	0.42
Cr	93.6	0.32	90.7	1.47
Ca	88.1	1.30	110.6	0.76
Mg	101.2	0.91	99.8	0.67

2.5　元素含量讨论

从实验结果来看，秦艽和麻花秦艽均富含 Ca，Mg，Fe，Mn，Zn 等元素，Ca 的含量最高。Ca 可加强大脑皮层的抑制过程，调节兴奋和抑制过程的平衡失调，还有消炎、消肿抗过敏作用以及解毒作用[16]，这与秦艽抗炎的药理作用相一致。Mg 具有舒张血管而使血压下降的作用，此与秦艽运用于心脑血管疾病具有明显疗效相一致。Fe 是血红蛋白和肌红蛋白中氧的携带者[17]，缺乏 Fe 会引起贫血，可造成各种器官的生理异常及生理变异。Mn 是多种酶的激活剂，是公认的抑癌元素[18]。锌参与 DNA 和 RNA 聚合酶，胸腺嘧啶核苷激酶，碳酸酐酶，碱性磷酸酶，胰腺羧基肽酶和乳酸脱氢酶等重要酶的合成[19]。有文献报道锌对类风湿关节炎有抗炎作用[20]，这与秦艽抗炎作用相一致。秦艽与麻花秦艽元素含量有所差异，其中秦艽中的 Ni，Fe，Mn，Mg 的含量高于麻花秦艽，而 Zn，Cu，Cr，Ca 的含量则是麻花秦艽高于秦艽。两者的差异，不仅与二者为不同种有关，而且可能与二者生长的生态环境有关。

中药微量元素是临床防病治病的重要物质基础之一。中药微量元素含量不仅为中药材质量控制提供了一定的理论依据，也为进一步研究中药作用机理，开发新药资源，研制新药提供了一定的信息和基础。

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Determination of Trace Elements of Gentiana Macrophlla and Gentiana Straminea by Microwave Digestion-FAAS

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Abstract An acid-assisted microwave digestion procedure is optimized for the determination of trace elements in traditional Chinese medicine by the use of flame atomic absorption spectrometric (FAAS) techniques. Microwave-assisted digestion has the advantages of reduced time for sample dissolution, fewer possibilities for technical errors caused by spilling of hot digestion solutions, use of less chemicals, and lower losses of volatile metals. In addition, modern microwave ovens are safer and simpler and provide more controlled and reproducible conditions than hot plate or block digesters. Flame atomic absorption spectrometry (FAAS) is more commonly applied techniques in the de termination of trace elements. The accurate measurement of trace elements concentrations in samples of traditional Chinese medicine is an important goal in research for medical effects of traditional Chinese medicine. The purpose of this study was to determine the contents of the trace elements in *Gentiana macrophlla* and *Gentiana straminea*. In order to identify the accuracy of the procedure, the operating conditions was selected before the determination of trace elements. In order to gauge the effectiveness of digestion, the selection of digestion conditions of the technique was undertaken. The results showed HNO_3-H_2O_2 (5∶1) as a microwave digestion agent with suitable temperature and time was optimum choice in the digestion procedure. Analysis limits were also selected according to the low detection limits and the good precision. They were Fe(248.3 nm), Mn(279.5 nm), Ni(232.0 nm), Cu(324.8 nm), Zn(2.139 nm), Ca(422.7 nm), Mg(285.2 nm) and Cr(357.9 nm), respectively. The working curves were obtained by using multi-elemental standard solutions and line relation was good. Under the selected conditions, the contents of trace elements Fe, Mn, Ni, Cu, Zn, Ca, Mg and Cr in *Gentiana macrophlla* and *Gentiana straminea* were directly determined using working curve methods. The relative standard deviations (RSD) and recovery of the method have been undertaken to obtain reliable results for trace element determinations. The recovery rates obtained by standard addition method were between 88.1%-114.5%, and the relative standard deviations (RSD) were lower than 3.12% after optimization of the o perating conditions. These figures showed that the method gave good recoveries and accuracy. The analytical results indicated that there were comparatively rich elements in *Gentiana macrophlla* and *Gentiana straminea*, such as Ca, Mg, Fe, Mn and Zn, especially the concentration of Ca and Mg. However, concentrations of Ni and Cr in *Gentiana macrophlla* and *Gentiana straminea* were very low, especially the concentration of Ni. The worse value obtained for Ni was probably due to its inhomogeneous distribution and very low concentration in *Gentiana macrophlla* and *Gentiana straminea*. In addition, a comparison of the contents of trace elements between *Gentiana macrophlla* and *Gentiana straminea* indicated that *Gentiana macrophlla* was rich in the trace elements such as Fe, Mn, Ni and Mg, and *Gentiana straminea* was rich in the trace elements such as Zn, Cu, Ca and Cr. The result will provide scientific datas for discussing the relationship between the contents of these elements in *Gentiana macrophlla* and *Gentiana straminea* and the medical effects. Furthermore, our study provides new scientific foundation for further study and general application of *Gentiana macrophlla* and *Gentiana straminea*.

Keywords Microwave digestion; Flame atomic absorption spectrometry; *Gentiana macrophlla*; *Gentiana straminea*; Trace elements

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