Asian Journal of Chemistry; Vol. 27, No. 6 (2015), 2049-2051

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17685

Determination of Chromium in Chinese Herbal Medicine with Matrix Modifier by Graphite Furnace Atomic Absorption Spectrometry

SHAOPING FENG[1,2], AIPING FAN[1,2], CHUN XU[1,2], WEI LIU[1,2,*], ZHAOLONG HUANG[1,2], SHIJUAN XU[1,2] and NA WU[1,2]

[1]School of Science, Honghe University, Mengzi 661199, Yunnan, P.R. China
[2]Key Laboratory of Natural Pharmaceutical and Chemical Biology of Yunnan Province, Honghe University, Mengzi 661199, P.R. China

*Corresponding author: Tel: +86 873 3694919; E-mail: liuwei4728@163.com

Received: 28 March 2014; *Accepted*: 18 June 2014; *Published online*: 17 March 2015; AJC-16957

A rapid analytical method of graphite furnace atomic absorption spectrometry has been developed for determination of chromium present in Chinese herbal medicine. The effect of digestion method on sample preparation was discussed and the determination conditions by graphite furnace atomic absorption spectrometry were optimized, with 2 % $(NH_4)_2HPO_4$ was used as matrix modifier, respectively. Under the optimum conditions, the linear range of chromium was 0 to 10 µg/L, the correlation coefficient was 0.9990 and the detection limit was 0.056 µg/L. The precision relative standard deviations were between 1.86 and 2.69 % for determining of chromium and the spike recoveries range from 97.47 to 101.90 %. These results indicated that the method is reasonable suitable for trace analysis.

Keywords: Graphite furnace atomic absorption spectrometry, Chinese herbal medicine, Chromium.

INTRODUCTION

Generally, Chinese herbal medicines contain many biologically active substances which have beneficial effects on human health as antioxidants and antibacterial compounds so that they are traditionally an important component of home remedies and raw materials[1,2]. However, Chinese herbal medicines may contain and cumulate heavy metals, especially chromium, which is extremely toxic to humans. Chromium affects on the mechanism of action of the insulin, the pancreatic hormone, taking part in glucose and fat metabolism[3,4].

Chinese national standards in the detection of the amounts of heavy metals in Chinese traditional medicine have not established[5]. With the frequent use of some herbal, to develop a convenient method for determination of the metals at the lowest possible levels with good precision and accuracy is an important and primary task because of the potential risk for human health. At present, Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is a widely used technique and adopted for measuring trace metals in different materials, as show low sensitivity for the determination of trace amounts of heavy metals in medicines[6-10].

In this research, we proposed a new and extremely high sensitive method, which is simple and expeditious for chromium determination by graphite furnace atomic absorption spectrometry, with 2 % $(NH_4)_2HPO_4$ as a matrix modifier.

EXPERIMENTAL

The atomic absorption spectrometer was SpectrAA 220 from Varian equipped with a GTA-110 graphite furnace and a programmable auto sampler. The instrument parameters are given in Table-1. Mechanical oven was equipped with temperature controller. Stock standard solution (1000 µg/mL) was obtained from the Chinese National Research Center of standard materials. All containers were cleaned with detergent and treated successively by the nitric acid and rinsed with de-ionized water.

Chinese herbal medicine was washed three times with de-ionized water and placed at blast oven dried at 60 ºC for more than 8 h, then smashed by the universal grinder, packed with a valve bag and placed in glass dryer.

High-pressure digestion: 0.5 g quantity of Chinese herbal medicine powder was transferred to a 100 mL high pressure bomb and 5 mL nitric acid, 3 mL 30 % H_2O_2 were added. The sample was allowed to stand for 12 h after which the sample was digested in high pressure bomb at 180 ºC for 5 h. Then the solution was heated until all the vapour turned from a brown to a white and the sample volume was allowed to reduce to about 1 mL followed by the addition of 3 mL of 30 % H_2O_2. The sample was reduced to approx 1 mL after heating and transferred to a 50 mL volumetric flask and diluted in 1 % nitric acid.

Wet digestion (HNO_3-$HClO_4$): 0.5 g quantity of Chinese herbal medicine powder was transferred to a 100 mL beaker

TABLE-1
INSTRUMENT PARAMETERS FOR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS)

Analytical condition	Parameters	Analytical condition	Parameters
Wavelength (nm)	357.9	Sample volumes	15 µL
Slit width (nm)	0.5	Matrix modifier volumes	5 µL
Background correction	Deuterium	Drying temp (°C)	120
Lamp current (mA)	5.0	Pyrolysis temp (°C)	1000
Argon (99.9 %) flow (L/min)	3.0	Atomization temp (°C)	2600
Measurement mode	Peak height	Cleaning temp (°C)	2700

and 10 mL nitric acid was added. The sample was placed on an electric plate with low temperature to digest and 4 mL nitric acid, 1 mL $HClO_4$ were added after cooling. The solution was heated many times with the same method until it was transparent. Then the solution was transferred to a 100mL volumetric flask and diluted in 1 % nitric acid. The digestion method (HNO_3-H_2O_2) is similar to HNO_3-$HClO_4$ method except standing for 12 h when the nitric acid was added.

Dry digestion: 0.5 g quantity of Chinese herbal medicine powder was transferred to porcelain crucible and placed on an electric plate with low temperature until the smoke disappeared. The sample was then placed at muffle furnace at 500 ºC for 4 h and 5 mL nitric acid was added after cooling to dissolve completely. Finally, the solution was transferred to a 100 mL volumetric flask and diluted in 1 % nitric acid.

The graphite furnace atomic absorption spectrometry analysis condition is listed in Table-1. The Chinese herbal medicine powder samples were digested with high-pressure and the measurement was repeated two times and the obtained signals were averaged.

RESULTS AND DISCUSSION

Linear regression equation and limit of detection: To prepare the standard solution, an aliquot (1 mL) of stock standard solutions (1000 µg/mL) of chromium was transferred into a 100 mL volumetric flask separately. The standard solutions were diluted individually with 1 % (v/v) nitric acid to get desired working concentrations, which were as follows: 2, 4, 6, 8, 10 µg/L. The linear regression equation obtained was A = 0.0244C + 0.0163 and the coefficient was 0.9990. Furthermore, the limit of detection was determined to be 0.056 µg/L based on a signal of eleven times the standard deviation of the blank.

Influences of digestion method: In this experiment, the effect of digestion method on sample preparation was discussed, including high-pressure digestion, wet digestion (HNO_3-$HClO_4$), wet digestion (HNO_3-H_2O_2) and dry digestion. The results are shown in Table-2.

The results given in Table-2 showed that chromium contents of high-pressure digestion is higher than that of wet digestion and dry digestion. So, the high-pressure digestion method was used to digest the Chinese herbal medicine samples in subsequent experiment.

Influences of matrix modifier: Graphite furnace atomic absorption spectrometry analysis method often subject to matrix interferences that can increase the ashing temperature and can be measured at the same time to eliminate the element loss caused by molecular absorption[11,12]. In this study, five matrix modifiers, *viz.*, 5 g/L $(NH_4)_3PO_4$, 5 g/L $(NH_4)_2HPO_4$, 5 g/L $NH_4H_2PO_4$, 5 g/L $Mg(NO_3)_2$ and 10 mg/L $PdCl_2$, were used to eliminate interferrent in order to improve the sensitivity measure of 5 µg/L Cr (Fig. 1). Subsequently, 2 % $(NH_4)_2HPO_4$ was selected as matrix modifier because of the higher absorbance.

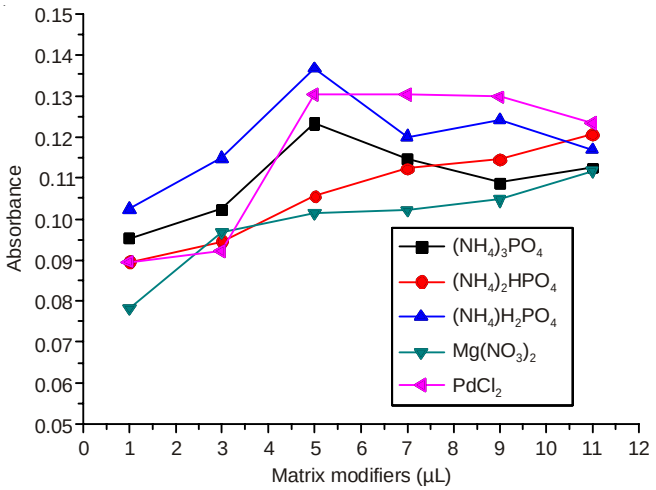

Fig 1. Effects of different matrix modifiers on absorbance

Effects of ashing and atomization temperature: Usually a relatively high ashing temperature can be used to minimize the formation of potential and real interferences. Another, choosing the low atomization temperature not only eliminate interference and reduce the background absorption, but also prolong the life of graphite tube on the condition that the absorbance was not reduced. The effect of ashing temperature and atomization temperature on the determination of 5 µg/L Cr is shown in Fig. 2.

TABLE-2
DETERMINATION RESULTS OF DIFFERENT DIGESTION METHOD (µg/g)

Samples	High-pressure digestion	Wet digestion HNO_3-$HClO_4$	Wet digestion HNO_3-H_2O_2	Dry digestion
Panax notoginseng	0.2164	0.2069	0.1967	0.1894
Saussurea costus	0.3151	0.2972	0.3014	0.2797
Rhizoma paridis	0.2457	0.2254	0.2317	0.2314
Poria cocks	0.4871	0.4790	0.4922	0.4781
Rhizoma coptis	0.1686	0.1524	0.1473	0.1569

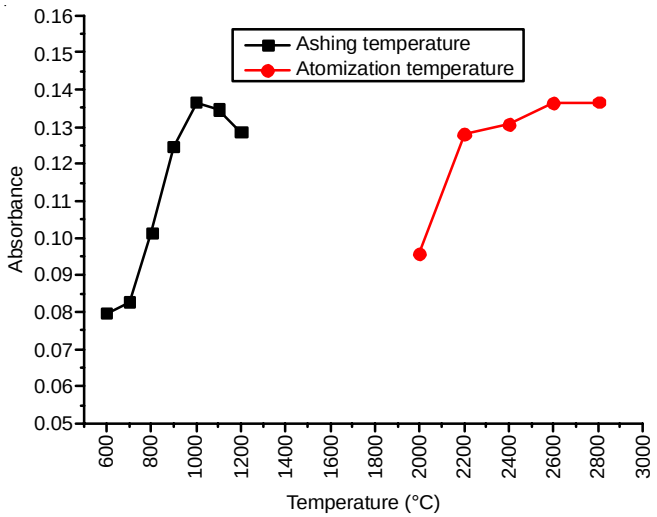

Fig. 2. Effects of ashing temperature and atomization temperature on absorbance

Fig. 2 showed that the absorbance of Cr increased in the range from 0.0797 to 0.1365 by increasing ashing temperature from 600 to 1000 ºC. Further increasing ashing temperature from 1000 to 1200 ºC, the absorbance of Cr reduced. Subsequently, 1000 ºC of ashing temperature was needed for determination of Cr. The absorbance of Cr increased in the range from 0.0958 to 0.1365 by increasing atomization temperature from 2000 to 2600 ºC. Further increasing atomization temperature from 0.1365 to 0.1367, the absorbance of Cr only had a slight increase (from 0.1365 to 0.1367). Subsequently, 2600 ºC of atomization temperature was needed for determination of chromium.

Interference experiments: The selectivity of proposed method was investigated by the determination chromium (5 µg/L) in the presence of various ions within a relative error of ± 5 %. The results showed that 20 % HNO_3, 5000 times Fe^{3+}, Na^{+}, Zn^{2+}, Al^{3+}, Mn^{2+}, 50000 times Cu^{2+}, Cd^{2+}, 100000 times Ca^{2+}, Mo (V) had no interference on the determination of 5 µg/L Cr.

Precision: As can be seen from Table-3, the precision relative standard deviations are between 1.86 and 2.69 % for analysis of chromium by this method, which was based on the prepared six digests.

TABLE-3
DETERMINATION RESULTS AND RELATIVE STANDARD DEVIATION (µg/g)

Samples	Average (µg/g)	RSD (%)
Panax notoginseng	0.2187	1.86
Saussurea costus	0.3218	2.48
Rhizoma Paridis	0.2467	2.61
Poria Cocks	0.4786	1.97
Rhizoma Coptis	0.1702	2.69

Recovery: The sample was added to different concentrations of standard solution to check the effect of sample matrix on determination of chromium. The recoveries of the results (Table-4) estimated in a percent average of the standard addition recoveries, were 97.47-101.90 %, which indicated that the method are reasonable suitable for trace analysis.

TABLE-4
TEST FOR RECOVERY OF CHROMIUM IN CHINESE HERBAL MEDICINE (µg/L)

Samples	Found 1	Added	Found 2	Recovery (%)
Panax notoginseng	2.16	1.00	3.21	101.58
		5.00	7.05	98.46
Saussurea costus	3.22	1.00	4.30	101.90
		5.00	8.17	99.39
Rhizoma paridis	2.51	1.00	3.46	98.58
		5.00	7.32	97.47
Poria cocks	4.75	1.00	5.63	97.91
		5.00	9.84	100.92
Rhizoma coptis	1.69	1.00	2.66	98.88
		5.00	6.71	100.30

Conclusion

Chromium in five different Chinese herbal medicine has been determined using graphite furnace atomic absorption spectrometry method with deuterium background correction. The Chinese herbal medicine were treated with high-pressure and the content of Cr has been determined under the condition of 2 % $(NH_4)_2HPO_4$ as matrix modifier with the volume of 5 µL, ashing temperature was 1000 °C, atomic temperature was 2600 °C. The proposed method is a precise, sensitive, simple, reliable, accurate technique and possesses lower limit of detection, which makes it suitable for the determination of trace amount of chromium in Chinese herbal medicine samples.

ACKNOWLEDGEMENTS

This work was support by Research of National Quality Inspection Standards of Nonprofit Industry in China (200810998) and the Chemistry of Key Construction Disciplines for Master Degree Program in Yunnan (HXZ1311).

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