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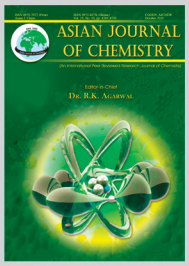

# Determination of Mineral Elements in Fifteen Medicinal Herbs and Their Infusions by Inductively Coupled Plasma Atomic Emission Spectrometry

QINGHUA YAN[1,*], LI YANG[2], HUIRONG ZHANG[2] and LIYUAN NIU[2]

[1]Department of Life Science and Technology, Xinxiang Medical College, Xinxiang 453003, Henan Province, P.R. China
[2]Department of Experimental Center, Henan Institute of Science and Technology, Xinxiang 453003, Henan Province, P.R. China

*Corresponding author: Fax: +86 373 3040015; Tel: +86 373 3831928; E-mail: yqh3499@yahoo.com.cn

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Nine mineral elements (Na, K, Ca, Mg, Cu, Zn, Mn, Se, Al) were determined in 15 medicinal herbs and their infusions consumed for people's daily lives and medicinal purposes in China. Microwave digestion procedure was applied under optimized conditions for dissolution of medicinal herbs. The concentrations of these mineral elements in the medicinal herbs and their infusions were determined by inductively coupled plasma emission spectrometry. The correlation coefficients (r) for all the analysis elements were showed in 0.9990-0.9999. The standard addition method was considered as a validation method of the accuracy and precision. Results showed the mineral and trace element content of medicinal herbs and their infusions displayed a wide variability, distribution of the elements in the medicinal herbs and their infusions was high for K, Na, Ca and Mg. However, some trace element concentrations in infusions were not high and they were very low or nil especially for Al, Cu, Mn and Se. The recovery of the element was 97-105 % and the RSD < 5.0 %. It is concluded that the present techniques are suitable for the routine determination of mineral elements concentration in medicinal herbs and their infusions. This study is to give important reference value to people due to individual differences by adjusting the herbal tea to complement the different trace elements.

**Key Words: Medicinal herbs, Mineral elements, Microwave digestion, Inductively coupled plasma atomic emission spectrometry.**

## INTRODUCTION

As concern people more of their health, Chinese traditional herb medicines play an important role in people's lives. Despite tremendous advances in synthetic medicinal chemistry, several diseases are not cured successfully due to their adverse side effects or diminution in response after prolonged use. In recent years, a global trend has been noticed for revival of interest in traditional herb medicines. A World Health Organization (WHO) survey indicated that about 70-80 % of the world population relied on non-conventional medicine, mainly of medicinal herbal sources in their primary health care. Continuous clinical research suggests that the balance of mineral elements in human body is disrupted by diabetes. Conversely, it has also been suggested that early imbalances of essential elements may play an important role in insulin metabolism[1]. Many plants are considered as an abundant source of essential trace elements and are prescribed because of their good bioavailability and least side effects, in addition to being of low cost[2]. Hence, medical doctors are also prescribing herbal teas and herbal extracts as a supplementary type of treatment in subhealthy problems caused by our modern life, for instance against stress or insomnia. The use of medicinal plants in both crude and prepared forms has greatly increased[3].

It is important not only to establish a method for determining the levels of some mineral elements (Na, K, Ca, Mg, Cu, Zn, Mn, Se, Al) in these medicinal herbs and their infusions that are widely and habitually consumed for medical purposes in China, but also to found a reliable analytical procedure on mineral elemens analysis. For example, simply employing a closed pressurized digestion system without optimizing the type and amount of reagents or heating temperature and program will not provide accurate and precise results. A number of techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemical methods, neutron activation analysis and total reflection X-ray fluorescence, instrumental neutron activation analysis (INAA) are widely used to determine mineral elements[4,5]. In this work, a closed-vessel, microwave digestion method for preparing fifteen medicinal herbs for ICP-AES analysis was described. Concentrated $HNO_3$ and $H_2O_2$ mixture were used as extractanted. Efficiency of the microwave extraction was evaluated by optimizing the conduction of microwave digestion.

The aim of the work is to determine mineral elements concentrations in fifteen medicinal herbs and their infusions by ICP-AES. Estimation of the amount of elements released from medicinal herbs into the water extracts can serve as a surrogate to people due to individual differences by adjusting the tea to complement the different mineral elements.

## EXPERIMENTAL

The samples of rabdosia rubescens tea, senna tea, semen cassiae, dwarf lilyturf, fios lonicerae, cape jasmine fruit, corn mint, chrysanthemum flower, Japanese pagodatree flower-bud, semen sterculiae lychnopherae, pericarpium citri reticulatae, indigowoad root, licorice root, semen coicies, wolfberry were purchased from a traditional Chinese medicine store in Xinxiang, China and authenticated by Yang li-juan (School of Pharmacy, Xinxiang Medical University, Xinxiang, China).

$HNO_3$ and $H_2O_2$ are analytical grade. All standard solutions used (0.00, 0.50, 1.00, 2.00, 4.00, 8.00 μg $mL^{-1}$) were prepared by diluting 1000 μg $mL^{-1}$ stock multi-element standard solutions (Na, K, Ca, Mg, Cu, Zn, Mn, Se, Al) with ultra-pure water for ICP-AES determination (Merck, Darmstadt, Germany). An ultra-pure water system (SG Ultra Clear system, Wasseraufbereitung and Regenerierstation GmbH, Germany), Optima2100 DV inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer Corporation of USA) and MAS microwave digestion system (CEM Corporation of USA).

**General procedure:** The samples were prepared by microwave digestion. The digestion was carried out in a PTFE vessel on 0.50 g of the dried herb sample by treatment with the mixture of 12 mL of concentrated $HNO_3$ and 2 mL $H_2O_2$. Microwave digestion procedure was applied under optimized conditions for digesting samples. After digestion, the sample was evaporated till near dryness, dissolved in water, transferred into a 25 mL volumetric flask, made up to the mark and shaken. The operational parameters of the microwave digestion was shown in Table-1.

TABLE-1
PARAMETER OF THE MICROWAVE DIGESTION

| Procedure | Power (W) | Raise of temperature time (min) | Work temperature (ºC) | Work time (min) |
|---|---|---|---|---|
| 1 | 400 | 8 | 120 | 3 |
| 2 | 800 | 5 | 150 | 5 |
| 3 | 1600 | 5 | 180 | 15 |
| Cool down | | | 70 | 20 |

To prepare the infusions of medicinal herbs, 0.50 g dried sample was placed in a beaker, then 25 mL of ultra-pure water at 95 ºC was poured into the same beaker and it was kept in water bath at 95 ºC for 10, 15, 20, 25, 30 min, respectively. After cooling, the infusion was filtered through the filter paper and the volume of infusion was filled up to 50 mL with ultra-pure water.

**Detection method:** Mineral elements were determined by ICP-AES. ICP-AES settings and operating conditions were shown in Table-2.

TABLE-2
ICP-AES OPERATING CONDITIONS FOR DETERMINATION OF SOME ELEMENTS IN MEDICINAL HERBS AND THEIR INFUSIONS

| Operating condition | Operating parameter |
|---|---|
| Rf power (W) | 1300 |
| Gas flow rate (mL $min^{-1}$) | |
| Coolant gas | 15 |
| Auxiliary gas | 0.2 |
| Nebuliser gas | 0.8 |
| Sample uptake rate (mL $min^{-1}$) | 1.5 |
| Torch | Fused quartz (radial) |
| Read time (s) | 15 |
| Delay time (s) | 30 |
| Wash time (s) | 30 |
| Elements monitored (wavelength, nm) | Na (589.59), K (766.49), Ca (317.93), Mg (279.08), Zn (213.86), Cu (324.75), Mn (257.61), Se (196.09), Al (396.15) |

## RESULTS AND DISCUSSION

**Optimization of the microwave digestion solutions:** Most digestion procedures for biological samples employ nitric acid because it is a strong oxidizing agent at high temperatures and concentrations. Additionally, nitric acid is easily purified and diluted solutions can be used for sample preparation step in order to increase the safety and to decrease reagent volumes and residues. Diluted nitric acid solutions were successfully used for microwave assisted plant digestion leading to low blank values[6]. If the concentrated $HNO_3$ was singly used in this study, it is impossible to dissolve such organic materials in medicinal herbs completely. All digestion solutions of medicinal herbs contained a slight precipitate even under optimized experimental conditions whereas colourless digestion solutions were the organic matter. Therefore, in order to enable the digestive more completely, $H_2O_2$ was used in all samples. When the value of $HNO_3$: $H_2O_2$ (v:v) was 12:2, digestion was provided completely.

**Infusion time:** In order to obtain the optimum infusion time, 10-30 min was examined. It was found that most of the mineral and trace element concentrations of the infusions were high in 20 min, but the per cent of Se in the herbs' infusions was high in 10 min. Moreover it was observed that the mineral and trace element concentrations in the sixteen medicinal herbs' infusions were not significantly changed after 25 min of infusion time.

**Linearity for the analysis elements:** The linearity for all the analysis elements by ICP-AES method was investigated under the above optimum analysis conditions. Calibration curves were obtained for analysis elements using a series of multi-element calibration standard solutions, A good linear relationship between the corresponding sensitivities and the concentrations of the analysis elements was achieved. The calculated regression equation, correlation coefficients (r) were showed in Table-3.

**Method validation:** In order to demonstrate the validity of the method, a recovery study was carried out. Semen coicis was selected to detect the precision and recovery with five parallel. Semen coicis was handled and the sample was determined following the recommended procedure. As can be seen

TABLE-3
LINEARITY FOR THE ANALYSIS ELEMENTS

| Element | Regression equation* | Correlation coefficient(r) | Element | Regression equation* | Correlation coefficient (r) |
|---|---|---|---|---|---|
| Na | Y = 2097654X – 193269 | 0.9993 | Cu | Y = 47624X + 1731 | 0.9999 |
| K | Y = 757235X – 74436 | 0.9990 | Mn | Y = 184725X + 5184 | 0.9999 |
| Ca | Y = 20572X + 9759 | 0.9993 | Se | Y = 1203X + 82 | 0.9991 |
| Mg | Y = 2839X + 201 | 0.9999 | Al | Y = 23516X + 471 | 0.9999 |
| Zn | Y = 128381X + 264 | 0.9999 | | | |

*Y = sensitivity (cps), X = concentration of compound (μg/mL)

TABLE-4
METHOD VALIDATION

| Sample | Element | Base value (mg/kg) | Quantity adde (mg/kg) | Quantity found (mg/kg) | Recovery (%) | RSD (%) |
|---|---|---|---|---|---|---|
| Semen coicis | Na | 18.00 | 5.00 | 22.85 | 97 | 0.71 |
| | K | 195.00 | 50.00 | 246.50 | 103 | 1.52 |
| | Ca | 22.00 | 10.00 | 32.20 | 102 | 0.79 |
| | Mg | 108.00 | 40.00 | 150.00 | 105 | 1.11 |
| | Zn | 1.90 | 1.00 | 2.93 | 103 | 0.45 |
| | Cu | 0.46 | 0.50 | 0.95 | 98 | 0.04 |
| | Mn | 2.00 | 1.00 | 2.97 | 97 | 0.47 |
| | Se | 0.18 | 0.20 | 0.38 | 99 | 0.05 |
| | Al | 2.20 | 1.00 | 3.17 | 97 | 0.51 |

in Table-4 the results are considered satisfactory. The RSD range from 0.04 to 1.52 %, recoveries being within the range: 97-105 %.

Concentration of elements in medicinal herbs and their infusions and the percent of element in the herb reported to infusion.

The concentrations of nine mineral elements determined in fifteen medicinal herbs and their infusions were collectively listed in Table-5. It also lists the percentage of each element reporting to the infusion. It was observed from the results of the test that all medicinal herbs contained significant values of elements and the content of elements in the medicinal herbs and their infusions presented a wide variability. Among the nine elements detemined in the study some of them are necessary to human health, such as Ca, Mg and Zn whereas the Al has been shown to be toxic. The other mineral elements are

TABLE-5
CONCENTRATION OF ELEMENTS IN HERBS AND THEIR INFUSIONS (MEAN ± SD mg/kg, n = 5)
AND THE PERCENT OF ELEMENT IN THE HERB REPORTED TO INFUSION

| Sample | Na | K | Ca | Mg | Zn | Cu | Mn | Se | Al |
|---|---|---|---|---|---|---|---|---|---|
| Rabdosia mbescens | 550.00 | 12743.54 | 10347.91 | 2679.41 | 34.99 | 11.78 | 86.08 | 0.45 | 337.82 |
| Infusion | 365.84 ± 36.02 | 11066.00 ± 58.11 | 2073.25 ± 51.60 | 956.19 ±16.40 | 5.62 ± 1.21 | 1.26 ± 0.64 | 16.09 ± 21.80 | Null | 23.86 ± 4.00 |
| Infusion (%) | 66.52 | 86.84 | 0.12 | 35.69 | 16.06 | 10.71 | 18.69 | Null | 7.06 |
| Senna tea | 1186.00 | 12534.93 | 35049.90 | 5163.81 | 11.83 | 7.14 | 36.18 | 1.75 | 185.11 |
| Infusion | 924.21 ± 30.11 | 9905.66 ± 90.10 | 22782.00 ± 49.10 | 4645 ± 11.30 | 8.77 ± 0.19 | 1.74 ± 0.51 | 25.55 ± 4.00 | 1.26 ± 0.42 | Null |
| Infusion (%) | 77.91 | 79.02 | 65.00 | 89.97 | 74.13 | 24.37 | 70.62 | 72.00 | Null |
| Semen cassiae | 3266.19 | 13792.07 | 6428.00 | 3255.33 | 42.82 | 10.31 | 17.23 | 1.79 | 26.34 |
| Infusion | 176.53 ± 13.19 | 4552.38 ± 53.00 | 1145.67 ± 60.00 | 536.72 ± 31.00 | 3.32 ± 0.43 | Null | Null | 0.47 ± 0.23 | Null |
| Infusion (%) | 5.41 | 33.01 | 17.82 | 16.47 | 7.75 | Null | Null | 26.26 | Null |
| Semen sterculiae lychnopherae | 989.00 | 22067.34 | 2711.11 | 2962.56 | 36.89 | 12.75 | 109.49 | 1.74 | 43.81 |
| Infusion | 670.00 ± 15.41 | 12905.32 ± 53.33 | 1114.00 ± 42.01 | 2548.00 ± 68.08 | 33.84 ± 1.76 | Null | 107.05 ± 11 | 121.00 ± 0.27 | Null |
| Infusion (%) | 67.75 | 58.48 | 41.09 | 86.01 | 91.73 | Null | 97.73 | 69.54 | Null |
| Licorice root | 302.91 | 7979.57 | 4881.96 | 1589.96 | 18.15 | 9.96 | 18.55 | 0.20 | 53.76 |
| Infusion | 225.75 ± 20.05 | 4800.25 ± 83.00 | 388.52 ± 60.50 | 387.00 ± 28.14 | 2.61 ± 0.39 | 1.55 ± 0.31 | 1.57 ± 2.07 | 0.10 ± 0.04 | Null |
| Infusion (%) | 74.53 | 60.15 | 7.96 | 24.34 | 14.38 | 15.56 | 8.46 | 50.00 | Null |
| Dwarf lilyturf | 533.62 | 11581.00 | 3295.96 | 465.36 | 10.37 | 4.05 | 8.48 | Null | 127.96 |
| Infusion | 330.00 ± 44.05 | 5353.00 ± 22.52 | 254.25 ± 15.30 | 139.00 ± 11.16 | 1.63 ± 0.21 | Null | 1.25 ± 0.14 | Null | 1.07 ± 1.24 |
| Infusion (%) | 61.84 | 46.22 | 7.71 | 29.87 | 15.72 | Null | 14.74 | Null | 8.38 |
| Pericarpium citri reticulatae | 230.68 | 10836.00 | 6412.43 | 1418.45 | 7.58 | 3.87 | 18.26 | 0.59 | 45.14 |

| Sample | Na | K | Ca | Mg | Zn | Cu | Mn | Se | Al |
|---|---|---|---|---|---|---|---|---|---|
| Infusion | 166.00 ± 4.03 | 6945.00 ± 29.00 | 1275.51 ± 90.12 | 526.00 ± 5.54 | 3.24 ± 0.72 | Null | 5.42 ± 2.27 | 0.30 ± 0.54 | 1.96 ± 0.08 |
| Infusion (%) | 71.96 | 64.09 | 19.89 | 37.08 | 42.74 | Null | 29.68 | 50.85 | 4.34 |
| Flos lonicerae | 385.00 | 28463.00 | 5991.24 | 4063.00 | 33.56 | 16.87 | 61.00 | 0.55 | 223.08 |
| Infusion | 338.00 ± 46.15 | 19876.03 ± 33.27 | 1373.21 ± 19.83 | 2191.00 ± 27.82 | 9.46 ± 0.31 | 6.97 ± 0.43 | 17.76 ± 3.21 | 0.49 | 2.52 ± 1.24 |
| Infusion (%) | 87.79 | 69.83 | 22.92 | 53.93 | 28.19 | 41.32 | 29.11 | 89.09 | 1.13 |
| Cape jasmine fruit | 278.07 | 27345.71 | 7329.89 | 2725.62 | 16.76 | 12.96 | 34.66 | 0.64 | 61.19 |
| Infusion | 184.00 ± 5.05 | 13923.00 ± 61.82 | 162.00 ± 4.52 | 440.00 ± 14.08 | 1.47 ± 0.82 | 0.87 ± 0.62 | 1.9 ± 0.21 | Null | 16.00 ± 7.00 |
| Infusion (%) | 66.17 | 50.91 | 2.21 | 16.14 | 8.77 | 6.71 | 5.65 | Null | 26.15 |
| Indigo woad root | 791.00 | 8172.00 | 4989.27 | 1552.18 | 25.14 | 2.36 | 13.23 | Null | 173.83 |
| Infusion | 496.52 ± 60.17 | 7389.33 ± 32.08 | 2099.08 ± 21.45 | 870.01 ± 50.01 | 10.69 ± 0.22 | Null | 4.34 ± 0.39 | Null | 9.94 ± 2.04 |
| Infusion (%) | 62.71 | 89.93 | 42.07 | 56.06 | 42.52 | Null | 32.81 | Null | 5.72 |
| Corn mint | 736.62 | 13529.16 | 11456.13 | 5217.26 | 18.44 | 15.25 | 48.16 | Null | 251.97 |
| Infusion | 588.27 ± 28.15 | 10657.33 ± 14.72 | 2951.42 ± 68.32 | 2744.56 ± 23.72 | 2.53 ± 0.21 | 2.42 ± 0.35 | 7.94 ± 0.67 | Null | 1.76 ± 1.49 |
| Infusion (%) | 79.89 | 78.62 | 25.76 | 52.59 | 13.72 | 15.87 | 16.49 | Null | 0.69 |
| Wolfberry | 4743.31 | 19880.94 | 1111.34 | 1125.32 | 18.68 | 12.84 | 14.55 | Null | 197.56 |
| Infusion | 3161.53 ± 96.08 | 13551.72 ± 30.05 | 605.76 ± 15.33 | 466.83 ± 11.04 | 7.48 ± 1.82 | 4.67 ± 1.25 | 3.54 ± 0.82 | Null | 5.45 ± 3.01 |
| Infusion (%) | 66.64 | 68.16 | 54.51 | 41.42 | 40.04 | 36.37 | 24.33 | Null | 2.76 |
| Chrysanthemum flower | 483.17 | 21708.15 | 6821.32 | 2415.01 | 37.24 | 15.98 | 48.91 | Null | 1279.62 |
| Infusion | 428.75 ± 28.17 | 16695.41 ± 30.09 | 2076.82 ± 12.35 | 925.91 ± 41.17 | 4.82 ± 0.75 | 4.67 ± 1.24 | 13 ± 3.02 | Null | 55.97 ± 3.34 |
| Infusion (%) | 88.77 | 76.91 | 30.43 | 38.31 | 12.94 | 29.22 | 26.58 | Null | 4.44 |
| Pagodatree flower-bud | 361.23 | 25376.11 | 9640.55 | 3566.31 | 41.64 | 20.05 | 45.35 | Null | 215.29 |
| Infusion | 328.54 ± 32.02 | 20215 ± 30.09 | 2043.22 ± 11.36 | 1958.57 ± 42.05 | 10.78 ± 1.21 | 6.03 ± 0.64 | 7.44 ± 0.14 | Null | 1.47 ± 1.02 |
| Infusion (%) | 91.45 | 79.66 | 21.19 | 54.91 | 25.89 | 29.93 | 16.41 | Null | 0.68 |
| Semen coicis | 224.48 | 2434.22 | 281.16 | 1348.60 | 23.69 | 5.83 | 23.84 | 0.64 | 27.35 |
| Infusion | 2.70 ± 0.51 | 1647.72 ± 17.05 | 77.64 ± 3.40 | 198.88 ± 15.13 | 1.26 ± 0.23 | 0.34 ± 0.20 | 2.72 ± 0.55 | 0.44 ± 0.31 | Null |
| Infusion (%) | 1.20 | 67.67 | 27.61 | 14.68 | 5.32 | 5.83 | 11.41 | 68.75 | Null |

n: number of assay for each of the medicinal herb sample; Null: not detected.

not toxic to human unless they are present in high concentrations. It must be noted that all of the medicinal herbs considered in this study are not cooked or consumed directly but are prepared as hot beverages such as tea. In spite of the fact that the concentration of elements such as K, Na, Ca, Mg and Al in the medicinal herbs seems high, they do not completely report to infusion. Therefore, comparing to the concentration in the medicinal herbs those in the infusions are more significant for taking into consideration the daily uptake.

## Conclusion

The proposed digestion technique is suitable for the application of microwave assisted extraction for the decomposition and dissolution of medicinal herbs for mineral elements determination by ICP-AES. In addition, purposed method is useful for routine control analysis of these products because of its rapidity, sensitivity and versatility.

Elemental contents vary in a wide range in the fifteen medicinal herbs and their infusions, in some cases even by an order of magnitude. This study is to give important reference value to people due to individual differences by adjusting the tea to complement the different trace elements.

## REFERENCES

1. A.Y. Oubre, T.J. Carlson and S.R. King, *Diabetologia*, **40**, 614 (1997).
2. C. Gopalan, B.V. Ramasastri and S.C. Balasubramaniam, Nutritive Value of Indian Foods, National Institute of Nutrition, ICMR, Hyderabad, India, p. 156 (1999).
3. D.M. Eisenberg, R.B. Davis and S.L. Ettner, *J. Am. Med. Assoc.*, **280**,1569 (1998).
4. H.X. Zhang and Y.K. Rui, *J. Saudi Chem. Soc.*, (in press).
5. Q.H. Yan, L. Yang, Q. Wang and X.Q. Ma, *J. Saudi Chem. Soc.*, (in press).
6. P.A. Reis and C.M.R. Almeida, *Food Chem.*, **107**, 1294 (2008).