THE CONTENT OF TRACE METALS IN SOME HERBAL TEA AND THEIR AQUEOUS EXTRACTS

KATARINA ČUNDEVA, MARGARITA SOTIROVSKA , TRAJČE STAFILOV
Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia; e-mail: trajcest@iunona.pmf.ukim.edu.mk

ABSTRACT

The contents of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in seventh herbal teas, from Macedonia, have been investigated by atomic absorption spectrometry. Two procedures for mineralization (wet and dry) are suggested. Procedures are checked by the method of standard additions. The results obtained reveal that trace metal contents vary markedly in different tea-samples. It has been shown that contents of investigated elements, with some exceptions, followed the pattern: Fe>Mn>Zn>Cu>Ni>Cd>Co>Cr>Pb. Variations in the amounts of some elements are probably due to various time period of the plant collection, various origin, as well as to differences of species included in the examination. Trace element content depends of climatic, ecological, pedological and other factors. The content of each element that was achieved in the aqueous extracts prepared from herbal teas was also investigated and the results show that they varied considerably and did not correspond to those in the herbal material. In the most cases the content of elements in the extracts was in the following order Mn>Zn>Fe>Cu>Cd>Co>Ni>Pb>Cr.

Keywords: Heavy metals, medicinal plants, determination, atomic absorption spectrometry

INTRODUCTION

As acknowledged, a great number of analytical works has been devoted to the determination and distribution of trace metals changes in their concentration and possible contamination in a wide range of different materials from agricultural to environmental science (Holak, 1980; Gambi et. al., 1982; Roy et al., 1993). However, the control of health fitness of medicinal plants demands the systematically monitoring and supervision of some pollutants' levels, including toxic elements (Official letter of SFRJ 59/1983). The presence of trace elements in the plants is expected in a small quantity. As a result of polluted environment their concentrations can be increased, and elements which are not naturally present in the plant constitution can be found.

The most present contaminants are Pb and Cd. Their toxical reaction takes origin of their specific influence mechanism, which disturbance can spoil the hemoglobin synthesis and in that case anemia appears (Casarett and Doull, 1986). Many factors influence the trace metals content in plants, for example availability and mobility of the trace elements in the soil, pH value of soil, humidity, environmental factors (Roy et al., 1993), genetic predisposition, time of sampling, plant part, influence of herbicide treatment (Shovljanski et al., 1989) and others.

Our work has been conducted upon the determination of some microessential (Fe, Cu, Mn, Zn Co, Cr and Ni) and toxic elements (Pb and Cd) in several medicinal and fruit plants grown in Macedonia and most commonly used in traditional herbal medicine. Also

some macroelements (Ca, Mg, Na and K) were determined. The contents of microessential and toxic elements in aqueous extracts have been also investigated. The determinations of trace elements have been performed by atomic absorption spectrometry (AAS).

MATERIAL AND METHODS

Plant material

The investigated medicinal plants available on the home market are given in Table 1. They are produced in Macedonia and have been used in different medicinal (sample No. 1-5) or refreshment (sample No. 6 and 7) purposes.

Table 1. Investigated medicinal and fruit plants

Sample No.	Plant species	Plant part
1	Alkalax – *Sennae folium*	Aerial part
2	Camomile Tea – *Chamomillae flos*	Aerial part
3	Linden Tea – *Tiliae flos*	Flower
4	St. John's Wort Tea - *Hiperici herba*	Aerial part
5	Wild Thyme Tea - *Serpylli herba*	Aerial part
6	Orange Tea - *Citrus aurantium*	Bark
7	Strawberry Tea - *Fragaria ananassa*	Leaves

Plant preparation

Two procedures have been applied for plant preparation.

Procedure 1: Aliquots of dried milled plant samples were dry-mineralized in a porcelain crucible at a temperature of 250 °C for 6 h and of 450 °C for one hour in a muffle furnace. The obtained residues, after cooling at room temperature were, dissolved in 100 mL of 4% HNO_3. From this solution, Fe, Mn and Zn were analyzed directly, and by flame atomic absorption spectrometry (FAAS) and the other metals were analyzed by electrothermal AAS (ETAAS).

Procedure 2: Aliquots of dried milled plant samples were mineralized by a mixture of HNO_3:H_2O (1:1/*V:V*), for several hours in a porcelain crucible. Further, mineralization was carried out by adding a concentrated H_2SO_4 and H_2O_2 (1:1/*V:V*). Thereafter, the samples were mineralized at a temperature of 400-420 °C in a muffle furnace. The obtained residues were dissolved in the 100 mL of 4% HNO_3. Blank samples were prepared in the same way as described above.

Preparation of aqueous extracts: The aqueous extracts of the plant material were prepared when 5 g of plant material were soaked in 100 mL boiling deionized water and left to stay for 15, 30 and 60 min. After 10 min. it was filtered off. Thereafter, the plant material was discarded. Investigated elements were analyzed directly from the filtrate.

Instrumentation

A Perkin-Elmer 1100 atomic absorption spectrophotometer equipped with Perkin Elmer HGA-400 graphite furnace was used. The light sources were hollow cathode lamps. Pyrolytically coated graphite tubes were used. The optimal operating conditions for Fe, Mn, Zn, Ca, Mg, Na and K determination by flame AAS and for electrothermal AAS (ETAAS) determinations of Cd, Co, Cr, Cu, Ni and Pb are given in Tables 2 and 3.

Table 2. Optimal instrumental parameters for the determination of Fe, Mn, Zn, Ca, Mg, Na and K by FAAS

Element	Wavelength/nm	Spectral slit/nm	Lamp current/mA
Fe	248.3	0.2	20
Mn	279.5	0.7	20
Zn	213.3	0.7	15
Ca	422.7	0.7	7
Mn	285.0	0.7	4
Na	589.0	0.2	6
K	766.5	2.0	12

Table 3. Optimal instrumental parameters for ETAAS measurements

ETAAS	Cd	Co	Cr	Cu	Ni	Pb
Wavelength, nm	228.8	240.7	357.9	327.4	232.0	283.3
Spectral slit, nm	0.7	0.7	0.7	0.5	0.7	0.5
Lamp current, mA	4	7	25	4	4	5
Calibration mode	Peak height					
Background correction	Deuterium					
Drying						
Temperature/°C	100	100	100	100	100	100
Time/s	25	25	25	25	25	25
Pyrolysis						
Temperature/°C	300	900	1000	400	900	900
Time/s	20	25	20	20	20	20
Atomizing						
Temperature/°C	2100	2300	2100	2100	2400	2300
Time/s	6	6	6	6	6	6
Cleaning						
Temperature/°C	2500	2400	2200	2200	2500	2400
Time/s	5	5	5	5	5	5
Cleaning gas	Argon					

RESULTS AND DISCUSSION

Mineralization of the plant material is very important phase in the determination of metals by AAS. There are different approaches to the process of mineralization, but in general dry (Isaac and Johnson, 1975; Haynes, 1980; Shovljanski et al., 1990; Panovska et al., 1995, 1997; Kadifkova Panovska et al., 1996, 1997; 1998) and wet (Panovska et al., 1997; Kadifkova Panovska et al., 1996, 1997; 1998) procedures are being applied. The results obtained by two methods are given in Table 4 (for macroelements) and Table 5 (for microelements). It was found that both procedures give satisfactory data but the method of dry mineralization has better precision. Because of that in further investigation Procedure 1 was used, except for Cd and Pb because of their easy evaporating features.

Macroelements (Ca, Mg, K, Na, Fe, Mn and Zn) were analyzed by flame (FAAS) and microelements (Cd, Co, Cr, Cu, Ni and Pb) by electrothermal atomic absorption spectrometry (ETAAS). The results obtained reveal that trace metal contents vary markedly in different tea-samples. The content of these elements is in accordance to previous data for different medicinal plat samples (Gambi et al., 1982; Shovljanski et al., 1989, 1990; Panovska et al., 1997; Kadifkova Panovska et al., 1996, 1997; 1998; Kulevanova et al.,

1998; Slaveska et al., 1998). It has been shown that contents of investigated macroelements, with some exceptions, followed the pattern: K>Ca>Mg>Na>Fe>Mn>Zn. For microelements the content decrease as followed: Cu>Ni>Cd>Co>Cr>Pb. The presence of Pb and Cd indicates a sort of certain contamination, but the content of Cd in all samples included in our examination was in these limits. Variations in the amounts of some elements are probably due to various time period of the plant collection, various origin, as well as to differences of species included in the examination. Trace element content depends of climatic, ecological, pedological and other factors.

Table 4. The content of macroelements (Ca, Mg, K, Na, Fe, Zn and Mn) in the investigated plant samples (in mg/g)

Sample	Ca	Mg	K	Na	Fe	Mn	Zn
Alkalax	28.73	5.06	8.27	2.06	0.351	0.031	0.046
Camomile Tea	5.42	3.53	19.96	3.13	0.220	0.083	0.075
Linden Tea	12.40	3.08	11.26	0.688	0.126	0.112	0.061
St. John's Wort Tea	4.68	2.55	14.61	0.686	0.581	0.248	0.104
Wild Thyme Tea	9.28	4.82	17.62	0.396	3.269	0.227	0.096
Orange Tea	5.66	2.23	10.33	0.302	0.103	0.120	0.072
Strawberry Tea	6.22	2.41	13.82	0.567	0.210	0.135	0.045

Table 5. The content of microelements (Cd, Co, Cr, Cu, Ni and Pb) in the investigated plant samples (in μg/g)

Sample	Cd	Co	Cr	Cu	Ni	Pb
Alkalax	1.36	0.79	0.54	3.85	6.37	0.08
Camomile Tea	1.16	0.34	0.34	9.30	2.02	0.13
Linden Tea	0.88	0.35	0.21	10.12	1.36	0.17
St. John's Wort Tea	1.09	0.53	0.46	4.50	1.31	0.26
Wild Thyme Tea	0.79	0.38	0.28	8.48	4.43	0.30
Orange Tea	0.61	0.28	0.19	1.89	9.67	0.12
Jag Strawberry Tea	0.25	0.94	0.10	7.30	3.63	0.30

The extractability of investigated elements in plant samples is given in Tables 6-9. The time of extraction was 15, 30 and 60 min. It was found that the highest extraction factors have Zn, Mn and Ca (from macroelements) and Cd, Cu and Pb (from microelements). The content of each element that was achieved in the aqueous extracts prepared from herbal teas was also investigated and the results show that they varied considerably and didn't correspond to those in the herbal material. In the most cases the content of elements in the extracts was in the following order Mn>Zn>Fe>Cu>Cd>Co>Ni>Pb>Cr. These results also show similar results, which were obtained for representatives of genus *Thymus* L. taken from different region in the Republic of Macedonia (Kadifkova Panovska et al, 1997).

Table 6. Extractability of Ca, Mg, K and Na in aqueous extracts (in %) after 15, 30 and 60 min of extraction

Sample	Ca			Mg			K			Na		
Time/min	15	30	60	15	30	60	15	30	60	15	30	60
Alkalax	17.5	21.0	23.3	4.0	4.2	4.9	2.7	3.6	-	2.6	3.1	3.5
Camomile Tea	26.2	26.4	26.9	4.8	5.1	5.2	4.8	5.3	6.3	0.5	0.6	0.8
Linden Tea	8.4	8.9	11.3	2.8	3.4	3.9	5.2	6.3	8.3	3.6	3.9	4.9
St. John's Wort Tea	15.7	19.8	37.4	4.9	5.0	5.1	3.6	4.2	4.5	5.2	5.9	6.8
Wild Thyme Tea	19.5	20.1	20.6	2.9	3.0	3.1	6.6	6.6	7.2	3.6	3.8	4.0
Orange Tea	10.9	12.0	15.3	7.4	7.9	8.4	8.5	8.5	10.6	5.1	5.2	5.3
Strawberry Tea	11.3	15.3	17.5	6.2	8.8	9.3	5.1	7.4	8.0	1.8	2.3	6.2

Table 7. Extractability of Fe, Zn and Mn in aqueous extracts (in %) after 15, 30 and 60 min of extraction

Sample	Fe			Zn			Mn		
Time/min	15	30	60	15	30	60	15	30	60
Alkalax	1.3	1.9	2.0	26.1	36.6	70.7	13.1	16.8	17.0
Camomile Tea	2.9	3.9	6.0	26.3	26.3	26.3	19.9	24.2	24.2
Linden Tea	4.2	4.9	6.7	20.0	25.3	25.9	11.8	16.9	19.1
St. John's Wort Tea	2.2	3.1	3.1	23.7	24.1	30.1	36.3	36.3	37.4
Wild Thyme Tea	0.5	0.5	0.7	16.3	17.5	20.1	15.1	15.1	15.1
Orange Tea	2.9	3.1	3.4	23.1	24.7	26.5	59.9	62.1	72.9
Strawberry Tea	1.2	1.3	1.5	38.7	54.6	71.1	33.5	68.2	73.2

Table 8. Extractability of Cd, Co and Cr in aqueous extracts (in %) after 15, 30 and 60 min of extraction

Sample	Cd			Co			Cr		
Time/min	15	30	60	15	30	60	15	30	60
Alkalax	13.5	38.7	54.4	2.6	4.9	6.1	4.2	5.5	4.8
Camomile Tea	50.2	49.4	51.0	23.1	23.4	29.5	6.2	9.2	7.1
Linden Tea	21.7	59.7	70.2	-	-	-	7.1	10.4	24.5
St. John's Wort Tea	12.3	9.3	14.5	9.2	10.9	-	3.0	20.1	49.9
Wild Thyme Tea	67.2	84.0	66.5	6.3	7.1	8.3	8.1	14.8	18.3
Orange Tea	90.6	66.7	54.2	19.6	42.3	53.0	38.1	46.4	81.0
Strawberry Tea	15.4	15.0	55.9	5.3	9.5	10.6	11.9	15.8	32.6

Table 9. Extractability of Cu, Ni and Pb in aqueous extracts (in %) after 15, 30 and 60 min of extraction

Sample	Cu			Ni			Pb		
Time/min	15	30	60	15	30	60	15	30	60
Alkalax	35.1	30.2	39.5	0.4	1.7	2.3	19.1	19.8	24.5
Camomile Tea	38.0	39.6	40.5	1.5	4.2	4.4	17.5	24.8	59.8
Linden Tea	19.0	20.0	20.8	2.3	3.7	3.8	11.1	17.4	28.2
St. John's Wort Tea	63.3	62.1	63.5	4.6	6.2	13.5	10.1	14.0	19.8
Wild Thyme Tea	17.0	20.0	20.5	3.1	4.1	6.9	6.7	12.8	29.6
Orange Tea	47.0	50.7	68.1	0.4	0.4	0.4	26.7	75.9	83.6
Strawberry Tea	11.4	12.8	19.7	1.2	2.2	3.1	10.1	28.3	34.7

REFERENCES

Casarett and Doull's Toxicology, The basic science of poisons, Third Edition. 1986. Macmillan Publishing Company, New York, pp. 609-619.

Gambi, V., Gabbrielli, R. and Pancaro L. 1982. Nickel, chromium and cobalt in plants from Italian serpentine areas. Acta Oecologica/Oecologica Plantarum, 3: 291-306.

Holak, W. 1980. Analysis of foods for lead, cadmium, copper, zinc, arsenic and selenium using closed system sample digestion: Collaborative study. J. Assoc. Off. Anal. Chem. 63: 485-495.

Haynes, R. J. 1980. A comparison of two modified Kjeldahl digestion techniques for multielement plant analysis with conventional wet and dry ashing methods. Commun. Soil. Sci. Plant Anal. 11:459

Isaac, R. A. and Johnson, W. C. 1975. Collaborative study of wet and dry ashing techniques for the elemental analysis of plant tissue by atomic absorption spectrophotometry. J. Assoc. Off. Anal. Chem. 58P:436

Kadifkova Panovska, T., Stafilov, T., Bauer, S., Kulevanova, S. and Dorevski, K. 1996. Determination of some trace elements in representatives of genus *Thymus* L. (*Lamiaceae*) by electrothermal atomic absorption spectrometry, Acta Pharm., 46:295-302.

Kadifkova Panovska, T., Stafilov, T., Bauer, S., Kulevanova, S. and Dorevski, K. 1997. Determination of Fe, Mn and Zn in representatives of genus *Thymus* L. by atomic absorption spectrometry, Arh. Farm., 5:598-599.

Kadifkova Panovska, T., Stafilov, T., Bauer, S., Kulevanova, S. and Dorevski, K. 1998. Determination of some macro and microelements in *Thymus moesiacus* velen. (*Lamiaceae*) and its water extracts by atomic absorption spectrometry, Ekol. Zašt. Živ. Sred., 5, 29-33 (1997).

Kulevanova, S., Kadifkova Panovska, T. Stafilov, T. and Lazaru, A. 1998. Heavy metals content in lime flowers from urban environment, Pharmacia (Sofia), 45:13-16.

Official letter of SFRJ 59/1983.

Panovska, T., Stafilov, T., Bauer, S., Kulevanova, S. and Dorevski, K. 1995. Determination of some macroelements in representatives of genus *Thymus* L. by atomic absorption spectrometry, Pharmacia (Sofia), 43:18-21.

Panovska, T., Stafilov, T. and Kulevanova, S. 1997. Determination of cadmium in representatives of genus *Thymus* (*Lamiaceae*) by electrothermal atomic absorption spectrometry, Anal. Lab., 6:158-162.

Roy, D., Greenlaw, P. and Shane, B. 1993. Adsorption of heavy metals by green algae and ground rice hulls. J. Environ. Sci. Health A28: 37-50.

Shovljanski, R., Lazic, S., Kisgeci, J., Obradovic, S. and Macko, V. 1989. Heavy metals contents in medicinal and spice plants treated with pesticide during the vegetation Acta Horticulturae 249, 51-60.

Shovljanski, R., Lazic, S., Mackō,V. and Obradovic, S. 1990. Heavy metals contents in medicinal and spice plants cultivated in Yugoslavia. Herba Hungarica 29:59-63.

Slaveska, R., Spirevska, I., Stafilov, T., Ristov, T. 1998. The contents of trace metals in some herbal teas and their aqueous extracts, Acta Pharm. 48:201-209.