Asian Journal of Chemistry; Vol. 23, No. 7 (2011), 3268-3272

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Determination of Copper, Iron, Manganese, Nickel and Zinc in Tea Leaf Consumed in Syria by Flame Atomic Absorption Spectrometry after Microwave Digestion

SAAD ANTAKLI[1,*], NAZIRA SARKIS[2] and AHMAD MAHMOD AL-CHECK[1]

[1]Department of Chemistry, Faculty of Science, University of Aleppo, Aleppo, Syria
[2]Department of Analytical Chemistry, Faculty of Pharmaceutics, University of Aleppo, Aleppo, Syria

*Corresponding author: E-mail: antakli@scs-net.org

(*Received*: 29 December 2010; *Accepted*: 26 March 2011) AJC-9777

The present work describes tea leave microwave digestion procedure by using new acid mixture (nitric acid and perchloric acid) for determining copper, iron, manganese, nickel and zinc in tea samples, employing flame atomic absorption spectrometry (FAAS). The optimization conditions involving the experiment factors: tea sample amount, microwave power and power time were studied for some kinds of tea consumed in Syria. The relative standard deviations of the method were found below 5 % for the 5 elements. The proposed method was used for the determination of the five elements in tea leave consumed in Syria for 39 tea samples. The obtained concentration of copper, iron, manganese, nickel and zinc varied between 10.6-54.4, 74.8-854.9, 225.1-1633.1, 1.1-16.3 and 18.0-44.2 (μg/g), respectively. These metals were also determined in tea infusion in boiled distilled water during (2-30 min) for three different samples. The percentage of the element contents in the infusion related to the total amount in tea leave were: zinc 19.71-28.34 %, manganese 11.79-26.95 %, iron < 5 %, copper and nickel were below the detection limit.

Key Words: Microwave digestion, Manganese, Iron, Zinc, Copper, Nickel, Tea, Tea influsion, Flame atomic absorption spectrometry.

INTRODUCTION

Tea is one of the heavily consumed beverages in the Syria which is prepared from the leave of a shrub camellia sinensis. It is also regarded as the most served beverage in the world[1]. It is grown in acidic soil widely from tropical to temperate regions. Various kinds of tea including black, green and herbal, *etc.*, are consuming at the high ratios. The chemical composition of tea leaves and manufactured tea are very complex and consists of tanning substances, flavones, alkaloids, proteins and amino acids, enzymes, aroma-forming substances, vitamins and 4-9 % inorganic matter[2,3].

The regular consumption of tea can contribute to the daily dietary requirements of traces of heavy metals including copper, iron, manganese, nickel, zinc, *etc.*[3].

A wide range of digestion methods for plants have been published such as dry digestion[4-6], wet digestion with different mixtures of reagents or conventionally heating procedures[7-15], digestion using an electromagnetic heating column[16] and microwave dissolution[3,12,17].

These methods generally showed relatively a good accuracy and precision. But the dry and wet digestion procedures take a long time[4]. Microwave digestion offers many advantages over conventional digestion procedures used for food analysis as: short time, acid use in a closed high-pressure polytetrafluoroethylene tube, does not lose any amount of the sample at the temperatures above the boiling point of nitric acid (good recovery)[3].

A wide range of techniques have been used for determining of trace heavy metals such as: inductively coupled plasma-atomic emission spectrometry (ICP-AES)[1], inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry, capillary electrophoresis (CE)[2] and graphite furnace (AAS-GF)[4,18]-flame atomic absorption spectrometry (FAAS)[3,7,10,11,16].

Flame atomic absorption spectrometry (FAAS) has been shown to be a promising technique for the determination of trace heavy metals in view of its low costs and easy usage[16].

EXPERIMENTAL

A Phoenix 986 AAWin V2.1 atomic absorption spectrometer with self-reversal background correction mode (SR lamp-BGC mode). The operating parameters for working elements were set as recommended by the manufacturer. The elements were determined by using air-acetylene flame. Microwave apparatus Ethod D (Milestone, Sorisole, Italy) with maximum pressure 1450 psi and maximum temperature 300 ºC.

All reagents used in the present work were an analytical reagent grade (Merck). Double distilled deionized water was

used for all dilutions. HNO_3 and $HClO_4$ were GR quality (Merck). All the plastic and glassware were cleaned by soaking in dilute HNO_3 and were rinsed with distilled water prior to use. The standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/L of the given elements supplied by (Merck).

The calibration curves for analyte metals were drawn after setting various parameters of FAAS including wavelength, slit width, lamp current at an optimum level.

Tea samples were purchased from supermarkets in Aleppo city-Syria in the year 2010.

The microwave digestions were carried out in the experimental heating program for the digestion procedure which is given in Table-1.

TABLE-1
HEATING PROGRAM FOR THE DIGESTION TEA LEAVE PROCEDURE

Step	Time (min)	Power (Watt)	Step	Time (min)	Power (Watt)
1	2	250	4	2	400
2	2	0	5	8	600
3	2	250	Ventilation	10	0

After the optimization of the digestion conditions, about 1 g of an oven-dried tea sample was put in microwave tube with 6 mL of concentrated HNO_3 and 2 mL of concentrated $HClO_4$ and placed in 70 ºC water path for 10 min, then it closed tightly and put in microwave to be digested by using heated program which is given in Table-1. The digested sample transferred to beaker and evaporated to about 5 mL, then transferred to volumetric flask 10 mL and completed to volume by distilled deionized water. A digested blank was carried out in the same way.

RESULTS AND DISCUSSION

Tea sample amount (TSA): Metals concentration was studied in relation to tea sample amount by using acid mixture (HNO_3-$HClO_4$) and reference digestion program[7]. The metals concentration in digested sample was constant until tea amount (1 g) (Table-2 and Fig. 1).

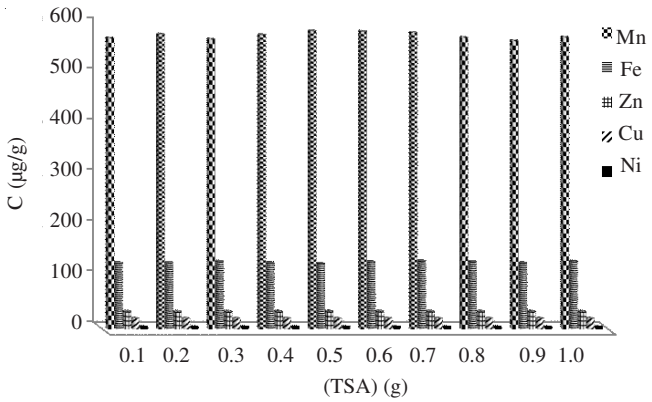

Fig. 1. Effect of tea sample amount

Microwave power (MP): Tea metals concentration was studied in relation to microwave power by using 1 g of tea leave. Expedience microwave power for a complete digestion was 600 watt. As it is given in Table-3 and Fig. 2.

TABLE-2
EFFECT OF TEA SAMPLE AMOUNT (TSA) N = 5

TSA (g)	Elements concentration (µg/g)									
	Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
0.1	4.00	6.1	21.10	5.4	35.00	3.2	130.51	3.5	574.00	1.3
0.2	4.05	5.7	21.00	4.8	34.50	3.4	131.42	3.4	581.50	1.6
0.3	4.00	5.4	20.83	4.6	34.66	2.6	133.54	2.9	571.66	1.2
0.4	4.15	5.1	21.25	4.7	34.75	3.1	130.71	4.1	580.25	2.3
0.5	4.16	4.9	20.80	4.2	34.80	3.0	129.20	2.4	588.00	2.1
0.6	4.03	4.4	21.45	4.1	35.16	4.1	132.54	2.6	586.83	1.4
0.7	4.01	4.8	21.14	3.6	35.14	3.6	134.18	3.1	584.57	3.1
0.8	3.93	4.2	21.16	3.0	35.00	3.2	133.23	3.6	575.00	1.4
0.9	3.94	3.5	21.11	3.1	34.77	3.5	130.41	3.8	568.33	2.4
1.0	4.05	3.6	21.08	3.0	34.70	3.4	133.40	3.4	575.40	1.8

N: Number of measurements for every sample.

TABLE-3
EFFECT OF MICROWAVE POWER (MP) ON TEA LEAVE METALS CONCENTRATION N = 5

(MP) (watt)	Elements concentration (µg/g)									
	Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
300	3.48	3.2	13.28	4.2	23.2	1.8	95.4	1.3	428.0	2.0
350	3.62	3.5	14.31	3.5	25.4	2.1	100.2	1.6	448.0	2.1
400	3.85	4.1	16.28	4.6	27.1	1.9	111.5	1.2	462.0	1.9
450	3.96	3.4	17.52	3.6	29.2	2.4	117.1	2.3	491.0	1.2
500	4.11	2.5	18.65	3.1	31.1	2.6	122.3	1.6	516.0	1.1
550	4.34	3.1	20.54	2.9	32.8	1.4	126.4	1.4	551.0	1.4
600	4.72	2.4	21.64	2.4	34.4	2.5	132.2	2.5	589.5	1.3
650	4.79	2.9	21.69	2.8	34.8	2.7	133.0	1.4	590.5	2.1
700	4.81	3.5	21.71	3.1	34.9	1.9	133.5	2.3	592.0	1.1

N: Number of measurements for every sample.

TABLE-4
EFFECT OF POWER TIME (PT) ON TEA LEAVE METALS CONCENTRATION (N = 5)

Power time (min)	Elements concentration (µg/g)									
	Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
2	3.08	4.1	18.0	4.2	31.9	1.6	86.2	2.3	579.5	1.3
4	4.04	3.2	19.0	3.5	33.1	1.9	95.6	2.0	584.5	1.6
6	4.90	3.4	21.8	4.6	35.3	3.2	125.2	1.6	586.5	2.1
8	4.84	2.9	21.5	3.6	34.9	2.1	133.7	1.5	598.0	1.1
10	4.57	2.6	20.4	3.1	34.6	2.5	132.5	1.6	595.5	1.2
12	4.54	3.1	20.2	3.2	34.5	2.0	133.1	1.4	596.4	1.3

N: Number of measurements for every sample.

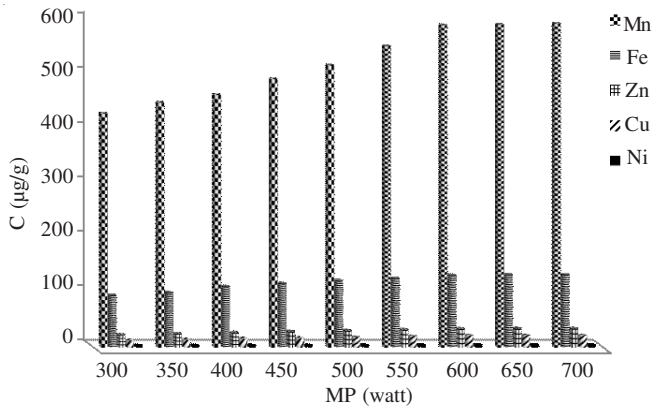

Fig. 2. Effect of microwave power on tea leave metals concentration

Power time (PT): Tea metals concentration was studied in relation to power time by using 1 g of tea leave and microwave power 600 watt. The expedience power time for a complete digestion was 8 min (Table-4 and Fig. 3).

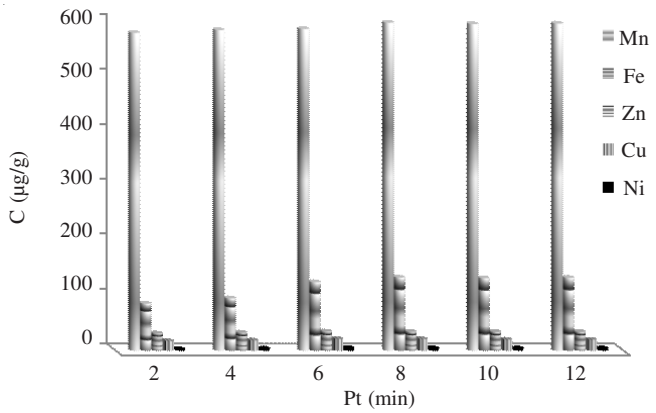

Fig. 3. Effect of power time on tea leave metals concentration

It is estimated that the recovery of copper, iron, manganese, nickel and zinc by using the addition-recovery test in the precedent optimal conditions (Table-5).

Application

Samples: The proposed microwave digestion procedure was applied for determining copper, iron, manganese, nickel and zinc in several tea samples, consumed in Syria, imported from much country as: Sri Lanka, China and Vietnam. The obtained results are presented in Tables 6-8. The concentration was found for copper, iron, manganese, nickel and zinc varied at 10.6-54.4, 74.8-854.9, 225.1-1633.1, 1.1-16.3 and 18.0-44.2 (µg/g), respectively.

TABLE-5
ADDITION-RECOVERY TEST FOR TEA SAMPLE (N = 5)

Element	Added (µg/g)	Found (µg/g)	Recovery (%)
Zn	0	20.50 ± 1.70	–
	40	59.20 ± 1.80	96.75
	60	78.00 ± 1.20	95.83
	80	97.80 ± 1.30	96.63
Cu	0	15.78 ± 1.90	–
	40	54.82 ± 0.67	97.60
	60	75.50 ± 0.63	99.53
	80	95.55 ± 0.73	99.71
Fe	0	136.50 ± 1.67	–
	80	215.80 ± 1.08	99.13
	120	256.20 ± 0.88	99.75
	160	312.40 ± 0.40	97.72
Ni	0	3.42 ± 5.26	–
	4	7.12 ± 4.40	92.50
	6	9.10 ± 4.06	94.66
	8	11.00 ± 2.92	94.75
Mn	0	486.46 ± 1.53	–
	200	684.14 ± 2.04	98.84
	400	885.21 ± 2.15	99.68
	600	1083.60 ± 1.25	99.52

N: Number of measurements for every sample.

Determination copper, iron, manganese, nickel and zinc in tea infusion: 2 g of dried tea leave (equivalent to one tea Sachet) was placed in a 250 mL of hot de-ionized water up to 90 ºC. The amount of manganese, zinc and iron in tea infusion was determined every 2 min until 10 min and every 5 min until 0.5 h for three tea samples. The infused percentage of metals to drinking tea was calculated. Blank experiments were carried out using hot de-ionized water up to 90 ºC. The obtained results are shown in Table-9.

Conclusion

The concentration of copper, iron, manganese, nickel and zinc in 39 various samples varied between 10.6-54.4, 74.8-854.9, 225.1-1633.1, 1.1-16.3 and 18.0-44.2 (µg/g), respectively. By comparison among the three countries of tea sources, it is observed that the Chinese tea leave content of each iron and manganese was the biggest. The amount of the elements contents in the metals infusion related to the total amount in leaves metals were: zinc 19.71-28.34 %, manganese 11.79-26.95 %, iron < 5 %, copper and nickel were below to the detection limit. It was observed that the biggest infused concentration of the zinc was at 10 and 8 min for the manganese. But the infused iron was negligible which assure its binding with the tea matrix.

TABLE-6
CONCENTRATION OF COPPER, IRON, MANGANESE, NICKEL AND ZINC IN CHINESE TEA, CONSUMED IN SYRIA

	Sample	Elements concentration (µg/g)									
		Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
Chinese green tea	1	8.70	4.15	18.35	4.19	35.32	1.68	268.20	3.65	1001.12	0.38
	2	3.44	3.65	16.17	3.06	35.14	2.11	431.18	2.38	1050.44	1.11
	3	3.66	4.59	16.00	5.18	35.54	3.05	541.94	1.50	1062.36	1.46
	4	5.04	1.86	14.52	2.30	43.04	1.96	98.44	3.83	649.90	1.07
	5	3.44	0.92	16.73	2.04	26.72	2.52	194.44	2.18	1400.88	2.68
	6	3.23	3.73	17.11	3.66	26.96	1.43	323.16	1.28	1449.88	2.88
	7	4.44	2.43	21.22	2.72	34.28	3.05	854.92	3.55	1204.10	2.03
	8	3.38	4.41	15.00	2.74	32.00	4.10	451.76	1.61	925.82	0.91
	9	5.22	2.54	22.98	2.16	35.70	1.60	426.00	3.46	1633.10	1.48
	10	4.66	2.68	12.34	4.26	21.40	3.80	420.76	4.56	573.00	2.31
	11	3.22	2.46	20.96	2.55	42.50	3.63	638.40	0.92	1445.72	1.31
	12	3.37	1.67	21.36	3.72	34.10	3.21	134.72	2.85	443.52	2.08

TABLE-7
CONCENTRATION OF COPPER, IRON, MANGANESE, NICKEL AND ZINC IN CEYLON TEA, CONSUMED IN SYRIA

	Sample	Elements concentration (µg/g)									
		Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
Ceylon black tea	1	16.30	6.43	54.46	4.74	35.32	2.76	128.36	2.85	374.88	1.99
	2	1.18	4.60	18.15	2.37	35.36	2.17	120.50	2.66	333.14	1.58
	3	2.68	1.98	17.80	4.69	31.00	3.13	110.78	2.76	435.96	1.01
	4	2.69	1.79	16.57	1.35	32.74	2.94	118.36	1.53	360.80	1.52
	5	3.48	1.93	17.57	5.05	35.64	2.49	104.44	2.44	486.46	1.58
	6	2.70	2.12	16.62	3.77	28.74	2.25	99.00	4.04	469.94	1.70
	7	3.54	2.64	20.05	2.27	31.64	3.26	107.68	2.36	434.06	1.66
	8	6.83	3.50	15.56	3.67	25.56	2.79	129.88	2.60	345.00	2.02
	9	3.54	2.84	16.68	1.18	32.80	2.16	123.08	2.99	379.04	2.97
	10	2.89	1.62	17.04	2.69	26.20	3.33	74.84	5.00	339.72	2.26
	11	8.59	1.79	12.11	2.79	24.28	5.96	187.68	1.61	1036.46	0.46
	12	3.51	4.99	22.24	3.10	36.60	2.31	150.32	1.77	251.84	2.54
	13	3.82	1.74	17.39	1.46	42.10	1.74	150.46	3.44	322.82	1.53
	14	2.21	3.29	15.54	0.66	26.10	2.45	123.14	3.24	391.04	1.71
	15	3.66	5.38	20.25	2.94	32.08	1.68	123.88	4.16	225.12	1.55
	16	2.31	4.49	15.33	3.21	25.34	2.58	110.06	3.22	335.54	1.00
	17	7.41	4.53	16.85	3.65	23.68	3.71	166.62	3.57	460.84	1.48
	18	3.53	2.61	19.11	3.24	25.54	2.62	96.14	2.71	407.48	1.00
	19	3.08	1.78	18.21	4.97	20.34	3.86	80.26	3.78	389.44	1.50
	20	3.34	4.82	18.13	5.14	30.00	4.86	88.60	4.91	436.90	1.87

TABLE-8
CONCENTRATION OF COPPER, IRON, MANGANESE, NICKEL AND ZINC IN VIETNAMESE TEA, CONSUMED IN SYRIA

	Sample	Elements concentration (µg/g)									
		Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	Fe	RSD (%)	Mn	RSD (%)
Vietnamese green tea	1	2.99	2.50	17.20	3.93	38.50	3.79	110.00	4.31	392.10	1.94
	2	4.90	4.64	14.59	2.81	25.08	5.25	347.16	4.38	555.80	2.38
	3	5.77	2.34	18.54	2.84	37.94	3.90	185.56	2.69	424.80	1.55
	4	5.33	4.12	17.76	2.72	26.76	3.05	362.76	4.66	865.40	2.47
	5	3.70	2.83	10.64	1.09	35.64	2.82	104.41	2.44	486.46	1.07
	6	4.05	1.46	10.62	1.11	24.48	2.41	159.34	2.87	455.56	0.84
	7	5.35	0.93	12.85	3.44	18.76	3.57	282.76	2.71	519.98	0.80

TABLE-9
INFUSED PERCENTAGE OF IRON, MANGANESE AND ZINC TO DRINKING TEA THROUGH 2-30 min

Sample	Time (min)	Zn			Mn			Fe		
		Tea leaf	Infused tea		Tea leaf	Infused tea		Tea leaf	Infused tea	
		Conc. (µg/g)	Conc. (µg/mL)	Transfer (%)	Conc. (µg/g)	Conc. (µg/mL)	Transfer (%)	Conc. (µg/g)	Conc. (µg/mL)	Transfer (%)
Ceylon number 12	2		0.061	20.83		0.429	21.29		0.03	< 5
	4		0.066	22.54		0.508	25.21		0.03	< 5
	6		0.071	24.24		0.519	25.76		0.04	< 5
	8		0.076	25.95		0.543	**26.95**		0.04	< 5
	10	36.60	0.083	**28.34**	251.84	0.547	27.15	150.32	0.04	< 5
	15		0.084	28.68		0.550	27.30		0.03	< 5
	20		0.086	29.37		0.547	27.15		0.03	< 5
	25		0.084	28.68		0.553	27.45		0.04	< 5
	30		0.085	29.03		0.558	27.70		0.03	< 5
Vietnamese number 5	2		0.040	14.04		0.640	16.44		0.03	< 5
	4		0.046	16.15		0.655	16.82		0.02	< 5
	6		0.052	18.25		0.691	17.75		0.02	< 5
	8		0.059	20.71		0.701	**18.00**		0.04	< 5
	10	35.64	0.061	**21.41**	486.46	0.709	18.21	104.41	0.03	< 5
	15		0.060	21.06		0.703	18.05		0.03	< 5
	20		0.062	21.76		0.710	18.23		0.04	< 5
	25		0.064	22.47		0.708	18.18		0.05	< 5
	30		0.065	22.82		0.705	18.11		0.05	< 5
Chinese number 3	2		0.029	10.21		0.861	10.13		0.02	< 5
	4		0.034	11.97		0.872	10.26		0.03	< 5
	6		0.046	16.19		0.901	10.60		0.02	< 5
	8		0.052	18.30		1.002	**11.79**		0.02	< 5
	10	35.14	0.056	**19.71**	1062.36	1.011	11.89	541.94	0.04	< 5
	15		0.055	19.36		1.013	11.91		0.03	< 5
	20		0.057	20.07		1.009	11.87		0.04	< 5
	25		0.056	19.71		1.014	11.93		0.03	< 5
	30		0.057	20.07		1.019	11.99		0.03	< 5

REFERENCES

1. W. Ashraf and A.A. Mian, *Bull. Environ. Contam. Toxicol.*, **81**, 101 (2008).
2. H.T. Feng, T.L. Wang and S.F.Y. Li, *Food Chem.*, **81**, 607 (2003).
3. M. Soylak, M. Tuzen, A.S. Souza and M. das G.A. Korn, *J. Hazard. Mater.*, **149**, 264 (2007).
4. S. Seenivasan, N. Manikandan, N.N. Muraleedharan and R. Selvasundaram, *Food Control*, **19**, 746 (2008).
5. S. Tautkus, R. Kazlauskas and A. Kareiva, *Chemija*, **15**, 49 (2004).
6. R. Street, *Czech J. Food Sci.*, **24**, 62 (2006).
7. P. Pohl and B. Prusisz, *Food Chem.*, **102**, 1415 (2007).
8. M.A. Herrador and A.G. Gonzalez, *Talanta*, **53**, 1249 (2001).
9. M. Yemane, B.S. Chandravanshi and T. Wondimu, *Food Chem.*, **107**, 1236 (2008).
10. S.B. Erdemoglu, K. Pyrzyniska and S. Gucerc, *Anal. Chim. Acta*, **411**, 81 (2000).
11. A. Mehra and C.L. Baker, *Food Chem.*, **100**, 1456 (2007).
12. I. Narin, H. Colak, O. Turkoglu, M. Soylak and M. Dogan, *Bull. Environ. Contam. Toxicol.*, **72**, 844 (2004).
13. M.A. Moghaddam, A.H. Mahvi, A.R. Asgari, M. Yonesian, G.H. Jahed and S.H. Nazmara, *Environ. Monit. Assess*, **144**, 23 (2008).
14. M.A. Taher, *Croat. Chem. Acta*, **76**, 273 (2003).
15. V. Naithani and P. Kakkar, *Bull. Environ. Contam. Toxicol.*, **75**, 197 (2005).
16. S.-P. Han, W.-E. Gan and Q.-D. Su, *Talanta*, **72**, 1481 (2007).
17. I. Narin and M. Soylak, *Anal. Chim. Acta*, **493**, 205 (2003).
18. G. Karimi, M.K. Hasanzadeh, A. Nili, Z. Khashayarmanesh, Z. Samiei, F. Nazari and M. Teimuri, *Pharmacologyonline*, **3**, 164 (2008).