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Metals Determination by Microwave Digestion ICP-OES of Some Dietary Supplements and Diet Products in Turkey

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ABSTRACT
Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was applied to metals concenrations in ten samples of some dietary supplements and diet products in Turkey. The As, Cr, Zn, Pb, Cd, Co, Ni, Hg, Mn, Fe, Al and Cu contents of dietary supplements and diet products were determined using microwave digestion. The digestion method with acid mixture (HNO_3 + HCl) was used to break down the organic material of dietary supplements and diet products. The results of analysis showed that the mean level of metals were Ni 3.34 ± 0.01 µg/g, Zn 41.24 ± 0.63 µg/g, Mn 23.27 ± 0.25 µg/g, Fe 221.10 ± 1.53 µg/g, Al 18.46 ± 0.14 µg/g and Cu 7.76 ± 0.15 µg/g for dietary supplements and diet products. The concentration of other metals and heavy metals was not found sufficiently. Based on the results obtained in the current work has sensitivity, and accuracy. Calibration curves showed a good linearity for all elements ($R^2>0.999$). The quantitation limit ranged 2.5 to 5 µg/L in dietary supplements and diet products. Recoveries were in the range 92.12-102.08%. The results obtained form this study have shown good accuracy and reproducibility.

Keywords: metal, dietary supplements, diet products, ICP-OES

INTRODUCTION

U.S. Food and Drug Administration (FDA) arranges dietary supplement products and dietary ingredients. In 1994, The US congress changed the Federal Food Drug and Cosmetic Act [1]. Under the Dietary Supplement Health and Education Act of 1994: Botanical products (Herbals), complementary nutritionals (amino acids, protein – rich foods, etc) and micrunutriens (vitamins, microminerals) are all considered to be dietary supplements [2]. Dietary products are used up to extend our diet with needed micrunutriens, herbs, protein and amino acid for ideal body function [3,4]. Different types of tea, pills and other similar products are sold to people over the internet for diet products. Diet products can be reached very easily. Today, the use of this product by people unconsciously lead to unintended consequences. Postmarketing reporting of adverse events by dietary-supplement

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manufacturers is required only for serious helth problems or fatal effects .Postmarketing regulatory process to recall dietary and diet products from the market or prohibition of sales from the internet hav ereceived public attention [5-7].

Dietary and diet products may be contaminated with heavy metals, microbial contaminants, pesticides, solvent residue and other toxins [8]. The use of 35 metals can cause problems to our health. We exposed of these metals in our residential or occupational life [9]. Identification and quantification determination of major-trace elements and heavy metals in dietary and diet products is very important for users of these products. Many trace elements play a important role in the formation of the active components are able for the therapeutic properties. However, these elements in high concentration can lead totoxic effects [10]. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Inhalation of heavy metals can be life threatening, cancer, rise to lung damage, gastrointestinal symptoms, disturbances of the cardiovascular or central nervous systems, hepatotoxicity, nephrotoxicity, and although acute pulmonary effects and deaths are uncommon, sporadic cases still ocur [11-14]

Several analytical methods have been used for the determination of major-trace elements and heavy metals in different products: The most commonly published techniques for the elemental analysis are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICPMS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma–atomic emission spectrometry (ICP–AES), charged particle induced activation analysis (CPAA), electrochemical methods, neutron activation analysis (NAA), photon activation analysis (PAA), total reflection X-ray fluorescence (XRF), energy dispersive X-ray fluorescence (EDXRF), and particle induced X-ray emission (PIXE) **[**8, 15-31].

However, in the literature, there are only several publications focused on the major-trace elements and heavy metals analysis of dietary and diet products [8, 15-31]. In this study, the concentration of some mineral elemets (Al, Cu, Fe, Mn and Zn) and some toxic elements (Pb, Cd, Hg, As, Cr, Co and Ni) in dietary and diet products were determined by ICP-OES. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). ICP-OES has clear advantatages in products multi element characteristics, speed of analysis and adequate detection limits.

EXPERIMENTAL

Equipment

Measurements was carried out with a sequential, axialy viewed Perkin Elmer Optima 8000 ICP-OES equipped with a meinhard nebulizer, a glass cyclonic spray chamber and ICP WinLab software Data System. The optimal conditions for ICP-OES are provided in **Table 2**. Analytical portions were digested with a microwave decomposition apparatus Milestone Stard D (Sorisole, Italy) equipped with temperature and pressure control to 200 °C and 45 bar, respectively. The microwave digestion system was capable of delivering 1450 W of maximum power with controlled temperature ramping. Microwave digestion vessels were lined and capable of operating at up to 200 °C and 45 bar). Ultrapure water was taken from a Sartorious Arium Ultra pure water purification system (Göttingen, Germany).

Materials

10 dietary supplements and diet products were examined. Two of the samples are in pill form. The eighty samples were in tea powder form. All samples were obtained from the internet in Turkey. With each set of digestions, a blank sample was simultaneously prepared through the complete procedure, analyzed and then used for correction of the analytical signals.

Reagents

The single component standards of lead (Pb), cadmium (Cd), copper (Cu), iron (Fe), zinc (Zn), arsenic (As), Chromium (Cr), Cobalt (Co), Manganese (Mn), Nickel (Ni), Aluminium (Al) and mercury (Hg) (each one with the content of 1000 ppm, Manchester New Hampshire). For the decomposition, analytical grade 65% w/v HNO_3 and 37% w/v HCl was used (Sigma Aldrich, Dermstadt, Germany).

Sample preparation

Prior to analysis, the samples were homogenised. Approximately 0.5 g of the sample was accurately weighed into an acid washed TFM digestion tube and 9 mL of HNO_3 (65% w/v) and 3 mL 10 M HCl were added [32]. The microwave oven condition lines are listed in **Table 1**. The maximum total out put of the microwave generator was 1450 W and the maximum pressure in the digestion tube was 45 bar. The digest was transferred into a 50 mL acid washed volumetric flask and the flask was filled up with ultrapure water and stored in a polypropylene container. Each sample was decomposed into three replicates. Two water blanks were run with each batch of samples.

Table 1. Microwave oven condition lines [33]

Step	Time	Temperature
1	15	110°C
2	15	110°C

The ICP–OES method

The measurement conditions were optimised based on the signal-to-back ground ratio of the least sensitive element (Mn). The measurement conditions are listed in **Table 2**. The selected analytical wavelengths are compiled in **Table 3**. The analyte emission was based on taking the difference of measured emission intensity on the top of the peak and back ground near the peak. All detection limits given by the ICP–OES software were based on three times

Table 2. Optimised operating conditions for the determination of constituents in milk by ICP OES

Rf power (W)	1450
Injector:	Alumina 2 mm i.d.
Sample tubing:	Standard 0.76 mm i.d
Drain tubing:	Standard 1.14 mm i.d.
Quartz torch:	Single slot
Sample capillary:	PTFE 1 mm i.d.
Sample vials:	Polypropylene
Source equilibrium delay:	15 sec
Plasma viewing:	Axial
Processing mode:	Peak area
Gases:	Argon and Nitrogen
Shear Gas:	Air

Table 3. Wavelengths Used and Plasma View Selected

Element	Wavelength (nm)	View
As	188.979	Axial
Cr	205.563	Axial
Zn	213.857	Axial
Pb	220.356	Axial
Cd	226.502	Axial
Co	228.612	Axial
Ni	231.604	Axial
Hg	253.652	Axial
Mn	257.610	Axial
Fe	259.943	Axial
Al	308.220	Axial
Cu	324.757	Axial

the Standard deviation of the background counts. Including the washing time between samples, the total time for analysis was approximately 7 min.

Hydride systems are used to enhance the detection of Hg and As.

Hg: 0.2% $NaBH_4$ (in 0.05% NaOH) + 3% HCl

As: 0.2% $NaBH_4$ (in 0.05% NaOH) + 10% HCl

Statistical analysis

Limit of detection (LOD), limit of quantification (LOQ), linearity of calibration, intra-and inter-day accuracy, precision and recovery were estimated for the validation of this method. Each element concentration was measured in three replicates. Samples with a mount below the LOD were not detectable. The extraction recovery and intraday precision of this method wered etermined by spiking blank milk with each compound in three replicates; they were

Table 4. In this research obtained data of LOD (μg/L) and r^2

Element	LOD	r^2
As	5.0	0.999
Cr	2.5	0.999
Zn	2.5	0.999
Pb	5.0	0.999
Cd	2.5	0.999
Co	2.5	0.999
Ni	2.5	0.999
Hg	1.0	0.999
Mn	2.5	0.999
Fe	2.5	0.999
Al	2.5	0.999
Cu	2.5	0.999

Table 5. Intra-day and inter-day precisions and avarage recovery

Compounds	Precision Intraday (n=3) (μg/L)			Precision Inter-Day (n=3) (μg /L)			Avarage Recovery (mean ± SD (%))
	10.00	25.00	50.00	10.00	25.00	50.00	
As	10.19	25.15	50.09	10.49	25.35	50.32	92.12 ± 2.22
Cr	10.07	25.03	50.02	10.48	25.31	50.29	98.00± 2.13
Zn	10.08	25.07	50.03	10.38	25.35	50.11	98.56 ± 3.30
Pb	10.13	25.10	50.09	10.13	25.15	50.10	100.21 ± 1.13
Cd	10.07	25.06	50.05	9.97	24.98	49.97	101.09 ± 1.98
Co	9.99	25.04	50.02	9.95	24.96	49.98	102.08 ± 4.23
Ni	10.06	25.12	50.09	9.93	24.95	49.96	95.65 ± 1.95
Hg	10.10	25.10	50.08	10.19	25.16	50.17	93.22 ± 1.55
Mn	10.06	25.04	50.05	10.28	25.21	50.16	98.89 ± 1.20
Fe	10.12	25.08	50.03	10.18	25.15	50.14	95.43 ± 2.75
Al	10.12	25.08	50.05	10.23	25.22	50.23	98.86 ± 1.78
Cu	10.11	25.04	50.03	9.96	24.95	49.97	97.43 ± 1.98

SD: Standard deviation

extracted as previously described. The inter-day precision and recovery were assessed by analyzing the target elements spiked at 5 different days.

RESULTS AND DISCUSSION

Analytical Results

When applied to dietary and diet products the proposed method showed good results. The calibration curves for all the species studied showed good linear correlation coefficients ($r^2>0.999$), independent of the method used for sample preparation. The detection limits (LODs) (calculated as 3 times the Standard deviation from 10 measurements of the blank) which are obtained for each method, are presented in **Table 4**. The quantitation limit ranged

Table 6. Levels (µg/g) of metals and heavy metals in dietary supplements and diet products

Sample	As	Cr	Zn	Pb	Cd	Co	Ni	Hg	Mn	Fe	Al	Cu
1	ND	ND	37.47 ± 0.02	ND	ND	ND	1.34 ± 0.01	ND	7.70 ± 0.02	204.50 ± 0.11	18.46 ± 0.14	5.13 ± 0.15
2	ND	ND	39.40 ± 0.03	ND	ND	ND	1.41 ± 0.01	ND	6.23 ± 0.07	19.14 ± 0.12	6.63 ± 0.11	6.13 ± 0.15
3	ND	ND	22.75 ± 0.10	ND	ND	ND	2.23 ± 0.01	ND	3.21 ± 0.12	79.67 ± 1.52	8.03 ± 0.01	3.33 ± 0.06
4	ND	ND	29.63 ± 0.11	ND	ND	ND	3.34 ± 0.01	ND	2.53 ± 0.03	88.11 ± 1.73	5.52 ± 0.05	3.86 ± 0.06
5	ND	ND	24.78 ± 0.15	ND	ND	ND	1.83 ± 0.02	ND	3.71 ± 0.02	44.00 ± 1.00	13.56 ± 0.05	7.76 ± 0.15
6	ND	ND	41.24 ± 0.63	ND	ND	ND	2.23 ± 0.02	ND	11.24 ± 0.13	46.97 ± 0.74	11.34 ± 0.08	6.80 ± 0.10
7	ND	ND	22.04 ± 0.09	ND	ND	ND	2.34 ± 0.06	ND	15.18 ± 0.03	221.10 ± 1.53	5.81 ± 0.05	5.78 ± 0.02
8	ND	ND	27.72 ± 0.25	ND	ND	ND	3.14 ± 0.06	ND	10.16 ± 0.15	153.70 ± 2.65	5.21 ± 0.18	5.68 ± 0.10
9 (pill)	ND	ND	11.61 ± 0.69	ND	ND	ND	1.77 ± 0.02	ND	23.27 ± 0.25	56.43 ± 0.51	16.57 ± 0.07	7.41 ± 0.10
10 (pill)	ND	ND	-	ND	ND	ND	1.83 ± 0.01	ND	-	-	-	-

ND: Not detected

2.5 to 5 µg/L in dietary supplements and diet products. The LOD 8.2 - 25 ng/L for metals were reported [19].

As a result, intra-day and inter-day precisions were adequate and avarage recoveries of studied metals and heavy metals were equal and higher than 92 %. Thus, this method seemed sensitive, precise and accurate for determining studied metals and heavy metals in dietary supplements and diet products samples. The recovery values 89-1001% for target metals were found [30].

Concentrations of metals and heavy metals in the dietary supplement products are shown in **Table 6** and represent the mean of three replicate analyses. The results of analysis showed that the mean level of metals were Ni 3.34 ± 0.01 µg/g, Zn 41.24 ± 0.63 µg/g, Mn 23.27 ± 0.25 µg/g, Fe 221.10 ± 1.53 µg/g, Al 18.46 ± 0.14 µg/g and Cu 7.76 ± 0.15 µg/g for dietary supplements and diet products. The concentration of other metals and heavy metals was not found sufficiently.

The concentration of Zn in dietary supplements and diet products ranged from 11.61 µg/g to 41.24 µg/g. The concentration of Ni in dietary supplements and diet products ranged from 1.34 µg/g to 3.34 µg/g. Nickel mainly comes through the poor quality fertilizers and micro nutrients [34,35]. The concentration of Mn, Fe, Al, and Cu in samples 2.53 µg/g to 23.27 µg/g; 19.14 µg/g to 221.10 µg/g; 5.21 µg/g to 18.46; 3.33 µg/g to 7.76 µg/g, respectively. Located value for Fe and Cu, according to the Turkish Food Codex.

Twelve elements consisting toxic metals and essential mineral elements were analyzed in ten dietary supplements and diet products using ICP-OES. The difference in metal concentrations may therefore be attributed to the contain different types of tea powder. Tea powders were provided from different regions. The last sample that does not include trace elements. Because it is not herbal.

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