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Determination of Trace Element Contents of Some Spice Samples by Using FAAS

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This study purposed to analyze the concentrations of 10 trace elements in aromatic spices (cinnamon, cumin, ginger, black pepper, red pepper and powdered pepper) by flame atomic absorption spectrometry (FAAS), after wet burning method. The analytical method was validated by linearity, detection limits, accuracy and recovery experiments values in all cases. The concentration of trace elements were measured in the range of 17.13–28.62, 3.09–8.57, 122.9–482.0, 492–999 and 28490–69630 mg kg^{-1} in order of zinc, copper, manganese, magnesium and calcium ions. As the toxic elemental contents were measured in the range of 1.61–14.06, 16.83–23.43, 27.03–56.07, 6.15–15.79 and 702–991 mg kg^{-1} in order of cobalt, lead, nickel, chromium and iron. The results were compared with the literature values. Pb, Ni, Fe and Cr elements are above the permissible limits and other elements are found to be at standard levels.

Keywords: Spice samples, Trace elements, Flame atomic absorption spectrometry, Method validation, Turkey.

INTRODUCTION

Spices are the store house of several elements over a large range of concentrations with significant positive or negative health effects. More than 20 elements have known physiological activities in humans and other mammals [1]. The metals vanadium, chromium, manganese, iron, cobalt, copper, zinc and molybdenum and the non-metals selenium, fluorine and iodine are trace elements that belong to the category of micro nutrients. This elements are required by the human body in small amounts (generally less than 100 mg/day). Other elements are considered to be macro nutrients, *e.g.* sodium, calcium, magnesium, potassium, chlorine, *etc.*, which are needed in larger amounts. Some trace elements are necessary ingredients of biological structures, however they can also be toxic at concentrations beyond those essential for their biological functions. Examples of these metals contain cobalt, copper, chromium and nickel [2]. Other elements like arsenic, lead and cadmium have well known toxic roles in various biochemical reactions [1,2]. For example, at trace levels, nickel is useful for the activation of some enzyme systems but, its toxicity at higher levels is more important. Fortunately, nickel toxicity in humans is not a very widespread event because the absorption of nickel is very little [3]. Trace elements are often conjugated in biological systems or connect to smaller molecules, like phosphates, phytates, polyphenols and other chelating compounds. Most of the metals in metalloproteins have structural functions in enzymatic systems or they use the protein to go to the targeted region in the organism [2]. For example, copper and zinc are used as activating agents for biochemical reactions and are components of some enzyme/substrate metal complexes [4]. Many spices are extensively used in Turkey and around the world in daily diet. Some of the benefits of these products are known as dementia fighting power (cumin), obesity and sugar regulating (cinnamon) and anticancer properties (turmeric). A lot of work has been done on the biological-activities and organic components of the aromatic spices, however less attention has been paid towards their minor and trace element contents. In view of the fact that these spices are being consumed in meals and as a supplement to give flavour in medical daily diets or as food. Identifying minor and trace element components of these spices is crucial for a clear understanding of the effects on human health [1]. Different techniques are used in determining minor and trace elements in the world, namely: differential pulse anodic stripping voltammetric technique [5], stripping potentiometry [6], capillary zone electrophoresis [7], instrumental neutron activation analysis [8], atomic fluorescence spectrometry [9], flow injection spectrometric methods [10], inductively coupled plasma emission spectroscopy [11], flame atomic absorption spectrometry [12], inductively coupled plasma optical emission spectrometry [13] and inductively coupled plasma mass spectrometry [14-17]. Flame atomic absorption spectrometry (FAAS) is a technique used for the detection of heavy metal ions at trace levels in environmental solid and liquid samples. It is also widely preferred because of its selectivity, low cost and easy tool handling

[18]. Even so, the analyte ions are at lower levels than the detection limits of FAAS and the high interference effects of ions on the analytes signal limit the determination of heavy metal ions by Gonzalvez *et al.* [19]. Therefore the aim of this study was to determine the concentrations of 10 minor and trace elements namely Co, Ni, Cr, Cu, Zn, Pb, Mn, Mg, Fe and Ca in six aromatic spices. The FAAS technique was used, because of its sensitivity, selectivity, trace levels and the ability to perform multi-element analysis. The critical levels specified by WHO and TGK were used to compare allowable maximum tolerable intakes of toxic trace elements.

EXPERIMENTAL

Red pepper, black pepper, powdered pepper, cumin, cinnamon and ginger samples were bought from market places at Karaman in Turkey. These were consisted of 16 samples from each of 6 selected spice samples as mentioned in Table-1. A total of 96 samples of spices were analyzed for their heavy metal contents. The samples were gathered in the summer and winter months and brought to the laboratory where they were packed. The region of the study were chosen from different potential pollution sources and unpolluted areas.

Sample preparation: All the samples were dried at 80 °C in oven until constant weight was achieved. These were homogenized in a blender (SS115, Warning, USA) and properly labeled. Spices samples were prepared for element analysis by the wet burning method [20,21]. Powdered spice samples (1 g) were put in 50 mL beakers and 15 mL of HNO_3 (65 %) (w/w) were added. After 8-10 h, 4 mL $HClO_4$ (70-72 %) (w/w) was added and heated gently for about 5-6 h and cooled. Then 5 mL of H_2O_2 (30 %) (w/w) was added and heated till the solution is colourless enough. The solution was cooled and distilled water was added in it until the total volume reaches to 15 mL.

A Perkin Elmer Model AAnalyst Pinaccle 900T atomic absorption spectrophotometer accoutred with deuterium back ground correcting and air-acetylene burner was used for Co, Ni, Cr, Cu, Zn, Pb, Mn, Mg, Fe and Ca measurements in standard and sample solutions. All elements hollow cathode lamps were used as radiation source. The most precision wavelengths (nm) and lamp currents (mA) used for the specification of the analytes were as follows: Co 240.7 and 30, Ni 232.0 and 25, Cr 357.9 and 25, Cu 324.8 and 15, Zn 213.9 and 15, Pb 217.0 and 440, Mn 279.5 and 20, Mg 285.2 and 20, Fe 248.0 and 30, Ca 422.7 and 20, respectively. The slit widths of Fe, Mn, Ni, Co elements are 0.2 nm and 0.7 nm for Cu, Zn, Ca, Cr, Mg and Pb elements. The absorbance measurements of all the elements were performed using an air/acetylene flame with a flow of 2.1-2.3 L min^{-1}. The nebulizer flow ratio and the burner height were set for obtain the maximum absorbance signal by aspirating asolution including the analyte in 0.05 mol L^{-1} nitric acid.

Analytical reagent-grade chemicals were employed in the preparation of all solutions. Doubly distilled deionized water (Milli-Q Millipore 18,2 MΩ cm^{-1}) was used in all experiments. The $HClO_4$, HNO_3 and H_2O_2 were of suprapure quality (Merck, Darmstadt, Germany). All the plastic and glassware were cleaned by soaking in dilute nitric acid and were rinsed with distilled water priorto use. The standard solutions of investigated analytes for calibration procedure were produced by diluting a stock solution of 1000 mg L^{-1} of the investigated element supplied by Merck. The plastic/glass containers were soaked in 10 % (w/w) HNO_3 for at least 24 h and then rinsed extensively with Milli-Q water prior to use. All the containers *i.e.*, polypropylene flasks, pipette tips and reagents that came into contact with samples or standards were checked for contamination. The Standard Reference Material (NIST), spinach leaves, was obtained from National Institute of Standards and Technology, Gaithersburg MD, USA.

Calibration procedure: The external calibration technique was followed for the quantitative analysis of the samples. Standard solutions were prepared in 19.6 % (w/w) HNO_3 by diluting a multi-element standard solution containing all the analyte elements. The calibration curves for all the analytes were built on 5 different concentrations of all analytes in the samples were within linear range of calibration curve. The calibration standards were analyzed at regular intervals during analysis as samples to monitor the instrument drift. Also ultra pure deionized water blanks were frequently analyzed along side samples to check for any loss or cross contamination. Any slight instrumental drift was taken into account to avoid any possible error. All the measurements were carried out using the full quantitative analysis mode.

Method validation: The analytical characteristic of the proposed method were obtained for the ten elements studied under the optimized conditions. Table-2 presents the linear ranges used for calibration and the coefficients of determination (R^2) used to assess the linearity ($R^2 > 0.99$). The limits of detection (LOD) and limits of quantification (LOQ) for each metal were determined as follows: 10 independent analyses of a blank solution spiked with the metal at a lower level of concentration of the analytical curve were performed. The LOD and LOQ were calculated from the standard deviation (σ) and the slope (m) of these determinations (LOD = 3 σ/m and LOQ = 10 σ/m).

TABLE-1
LIST OF AROMATIC SPICES STUDIED

No.	English name	Botanical name	Family	Part investigated
1	Cinnamon	*Cinnamomum verum*	Lauraceae	Bark
2	Cumin	*Cuminum cyminum*	Apiaceae	Fruits
3	Ginger	*Zingiber officinale*	Zingiberaceae	Fruits
4	Chili (red pepper)	*Capsicum annuum* L.	Solanaceae	Fruits
5	Chili (powdered pepper)	*Capsicum annuum* L.	Solanaceae	Fruits
6	Black pepper	*Piper nigrum* L.	Piperaceae	Fruits

TABLE-2
LINEAR RANGE, REGRESSION, CORRELATION COEFFICIENT (R^2), LOD, LOQ AND PRECISION (RSD %) FOR THE ELEMENTS ANALYZED

Element	Linear range (mg kg^{-1})	Regression	R^2	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Precision (RSD %)
Cu	1-10	y = 0.040x + 0.001	0.993	1.526	5.085	0.584
Cr	1-10	y = 0.012x – 0.002	0.996	2.497	8.324	0.715
Fe	1-10	y = 0.051x – 0.025	0.996	1.441	4.803	0.740
Ca	0.1-5	y = 16.10x – 0.108	0.999	0.053	0.158	0.117
Ni	1-10	y = 0.029x – 0.013	0.999	2.225	7.417	0.206
Mg	0.1-5	y = 2.106x – 0.106	1.000	0.108	0.360	0.727
Mn	0.1-5	y = 0.063x + 0.009	0.999	1.186	3.952	0.872
Zn	0.1-5	y = 0.137x + 0.002	0.993	0.784	2.612	0.355
Pb	1-10	y = 0.124x – 0.052	0.999	1.490	4.967	0.701
Co	0.1-5	y = 0.287x + 0.075	0.999	0.624	2.080	0.558

RESULTS AND DISCUSSION

The average results (concentration ± SD) of selected 10 minor and trace elements obtained for 6 analyzed spice samples using FAAS were reported on dry weight basis. Table-2 enlisted analytical method validation parameters including linear range, regression, correlation coefficient, LOD, LOQ and precision. Table-3 give analysis of SRM (NIST), for Cu, Cr, Fe, Ca, Ni, Mg, Mn, Zn, Pb and Co. Tables 4-9 give concentration (mg kg^{-1}) (average ± SD) of analyzed 10 trace elements in cinnamon, cumin, ginger, red pepper, powdered pepper, black pepper by FAAS, respectively (Fig. 1) average trace element (Cu, Co, Cr, Pb, Zn, Ni) contents of spices samples (mg kg^{-1}). Fig. 2 showed the average trace element (Mn, Mg, Fe) contents of spices samples (mg kg^{-1}). Fig. 3 depicts the average trace element (Ca) content of spices samples (mg kg^{-1}).

Toxic and non-toxic metals may occur due to contaminated soil and water, planting, growth and manufacturing processes in plant products. As toxic materials are probably to be present in many foods for their abundance in nature, the addition of vegetable products contaminated with metals also increases the total concentration of toxic metals consumed by humans [22]. The maximum amounts for toxic metals set by countries in different areas of the world have been published by the World Health Organization (WHO) in 2007. The limit of 10 mg kg^{-1} in raw herbal products and 0.02 mg day^{-1} in finished herbal products was determined for Pb. For chromium, the limit in crude herbal produce was 2 mg kg^{-1}; but, the limit in worked herbal produce is the same with lead, 0.02 mg day^{-1}. In spite of limits for toxic metals in plant products and drugs are generally determined for each element, some countries

TABLE-3
ANALYSIS OF CERTIFIED REFERENCE MATERIAL (NIST), BLANK (n = 3)

Element	Certified (mg kg^{-1})	Found (mg kg^{-1})	Recovery (%)	CRM NIST No.
Cu	2 ± 0.4	2.14[a] ± 0.01[b]	107.0	SRM 3114
Cr	2 ± 0.4	2.11 ± 0.02	105.5	SRM 3112a
Fe	2 ± 0.4	2.11 ± 0.02	105.5	SRM 3126a
Ca	10 ± 2	9.86 ± 0.01	98.6	SRM 3109a
Ni	5 ± 1	4.03 ± 0.01	80.6	SRM 3136
Mg	1 ± 0.2	0.98 ± 0.01	98.0	SRM 3131a
Mn	1 ± 0.2	0.99 ± 0.01	99.0	SRM 3132
Zn	1.8 ± 0.4	1.83 ± 0.07	101.6	SRM 3168a
Pb	20 ± 4	20.4 ± 0.14	102.0	SRM 3128
Co	2*	1.97 ± 0.01	98.5	–

*Value is not certified value.
[a]Average concentration of thirty replicate measurements.
[b]Standard deviation (n = 30).

TABLE-4
AMOUNTS OF TRACE ELEMENTS DETECTED IN CINNAMON SAMPLES BY FAAS ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Cinnamon	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	12.95	31.04	13.99	4.58	16.95	21.53	210.1	651	821	58920
	2	13.19	30.84	14.03	4.53	18.68	21.51	211.8	661	819	52220
	3	12.38	30.52	14.32	4.09	18.29	19.58	195.2	650	833	57120
	4	12.65	31.43	13.68	4.52	18.44	20.58	196.2	636	818	57100
	5	11.79	31.08	13.96	4.87	15.52	18.12	125.3	653	760	56980
	6	11.89	32.13	14.07	4.65	16.06	18.34	122.9	667	793	57080
	7	11.69	32.17	14.03	4.98	16.86	18.96	141.8	728	761	52500
	8	11.77	31.89	15.19	4.67	17.19	19.60	142.6	738	779	53700
Summer	9	10.29	30.98	14.56	4.65	17.53	18.00	187.5	650	807	49500
	10	10.35	32.12	14.57	4.86	17.91	18.30	184.3	658	826	50700
	11	11.85	31.56	13.98	6.87	16.84	19.15	186.9	662	884	48560
	12	12.07	31.66	13.97	7.11	15.68	19.37	192.8	666	839	49640
	13	11.89	31.65	15.16	5.59	17.35	21.04	172.8	636	825	44650
	14	11.67	31.81	15.15	5.71	16.53	21.88	174.8	648	833	45770
	15	11.76	29.42	12.77	4.77	17.23	19.87	142.9	699	888	45880
	16	11.56	32.33	13.72	4.97	16.95	20.03	152.9	613	873	45400
Average ± SD		11.86 ± 0.787	31.41 ± 0.430	14.22 ± 0.564	5.086 ± 0.861	17.13 ± 0.840	19.74 ± 1.284	171.3 ± 30.14	663.5 ± 29.10	822.4 ± 37.26	50920 ± 4637

TABLE-5
AMOUNTS OF TRACE ELEMENTS DETECTED IN CUMIN SAMPLES BY FAAS ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Cumin	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	11.60	32.19	7.15	5.35	25.18	17.57	391.6	568	920	31930
	2	11.90	32.31	7.24	5.47	25.99	17.04	416.8	588	899	31560
	3	12.48	34.28	7.29	5.43	25.79	16.83	413.2	688	967	28490
	4	12.66	34.55	7.91	5.23	25.23	19.46	412.3	686	978	28580
	5	12.04	33.14	7.72	4.42	22.58	18.86	321.9	577	914	36270
	6	12.22	33.37	7.94	4.63	23.78	19.99	333.7	572	949	35280
	7	11.17	32.43	7.15	4.05	22.81	18.93	332.0	536	852	35500
	8	12.20	33.14	7.67	4.13	23.02	19.64	333.7	533	868	33990
Summer	9	13.88	34.63	7.53	4.23	23.23	18.72	454.3	669	988	29840
	10	14.06	34.90	7.82	4.27	24.53	17.23	445.6	670	977	30640
	11	12.25	31.05	7.07	4.78	22.23	18.14	465.8	521	951	31200
	12	12.82	32.24	7.31	4.67	22.45	18.39	482.0	525	933	31520
	13	12.22	31.32	7.65	4.23	23.45	19.49	434.5	530	922	33910
	14	12.09	31.55	7.56	4.53	23.78	19.88	435.6	527	925	33910
	15	11.21	32.34	7.45	4.65	22.30	19.45	437.8	510	923	34910
	16	13.41	34.25	7.54	4.75	24.29	19.48	438.7	509	925	34700
Average ± SD		12.39 ± 0.717	32.98 ± 1.204	7.499 ± 0.227	4.675 ± 0.479	23.73 ± 1.076	18.69 ± 0.875	409.6 ± 52.80	575.6 ± 67.65	930.6 ± 37.79	32639 ± 2555

TABLE-6
AMOUNTS OF TRACE ELEMENTS DETECTED IN GINGER SAMPLES BY FAAS ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Ginger	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	12.28	36.75	15.11	5.79	18.95	20.14	234.2	819	744	65320
	2	12.86	34.56	15.21	5.96	19.01	21.51	236.0	807	748	69000
	3	12.38	35.66	15.79	5.32	18.89	20.61	233.4	814	813	66050
	4	13.25	35.47	15.23	5.59	20.02	20.51	236.8	810	815	66960
	5	12.43	36.65	12.29	6.58	18.56	20.41	203.8	808	704	64020
	6	12.29	36.35	12.33	7.18	18.76	19.34	224.9	809	726	64190
	7	12.25	35.60	10.98	7.26	18.65	17.26	278.3	832	782	69630
	8	12.42	37.25	13.11	7.42	18.45	19.72	206.0	841	709	68750
Summer	9	12.41	37.82	11.23	4.63	16.20	20.41	258.6	831	791	62970
	10	12.46	34.34	11.29	5.96	18.15	20.24	258.2	826	782	61420
	11	11.77	36.52	11.54	3.75	17.38	21.09	265.4	822	727	61630
	12	12.81	32.23	11.53	5.44	18.64	21.72	271.1	827	715	61490
	13	12.72	34.77	11.56	5.55	17.90	22.30	234.8	818	769	60950
	14	12.63	36.63	11.23	5.45	17.60	22.95	240.0	817	765	61640
	15	12.23	36.53	12.01	6.01	18.01	22.35	228.6	808	785	62750
	16	13.08	36.86	12.11	6.34	17.99	23.43	230.5	812	794	62260
Average ± SD		12.52 ± 0.188	35.87 ± 0.742	12.66 ± 1.693	5.886 ± 0.891	18.32 ± 0.732	20.87 ± 1.439	240.0 ± 16.77	818.9 ± 10.13	760.5 ± 34.85	64313 ± 2957

TABLE-7
AMOUNTS OF TRACE ELEMENTS DETECTED IN RED PEPPER SAMPLES BY FAAS ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Red pepper	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	11.68	32.36	8.18	4.79	17.56	20.45	369.0	654	912	33360
	2	11.90	34.11	8.02	6.41	17.43	19.01	379.7	660	912	32780
	3	11.69	34.88	8.01	6.62	17.41	19.64	377.5	694	999	35430
	4	12.49	35.53	8.99	6.73	17.57	19.90	395.0	696	998	34780
	5	11.81	35.47	6.15	4.15	16.73	20.61	235.4	730	702	30620
	6	11.93	32.31	6.62	4.49	17.77	19.92	237.5	737	901	39440
	7	10.93	32.81	6.58	4.15	17.84	20.64	212.2	809	841	32890
	8	11.82	32.52	7.19	4.16	18.40	19.95	221.3	808	802	33150
Summer	9	12.31	35.15	7.23	5.77	17.89	20.36	222.3	657	905	35060
	10	11.12	35.51	7.50	7.27	17.67	21.02	234.3	656	908	34660
	11	11.32	36.32	7.65	6.54	18.90	21.28	253.4	727	900	39880
	12	12.66	36.91	7.52	6.72	17.91	18.01	236.5	733	966	39300
	13	12.78	34.56	7.89	3.29	16.59	19.89	312.6	894	874	36470
	14	12.56	34.65	8.97	3.17	16.82	19.47	326.7	915	873	37020
	15	12.01	35.76	7.98	3.30	16.57	19.18	305.4	908	912	36150
	16	12.34	35.78	7.64	3.40	17.77	18.90	326.8	907	940	37860
Average ± SD		11.96 ± 0.381	34.41 ± 1.651	7.633 ± 0.738	5.061 ± 1.472	17.55 ± 0.543	19.83 ± 0.565	290.3 ± 67.65	761.5 ± 101.2	896.3 ± 63.92	34928 ± 2939

TABLE-8
AMOUNTS OF TRACE ELEMENTS DETECTED IN POWDERED PEPPER SAMPLES BY FAAS
ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Powdered pepper	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	10.41	27.03	12.59	5.14	23.45	19.50	198.7	869	848	49990
	2	10.92	30.17	13.56	5.26	23.48	19.48	201.0	873	853	51850
	3	10.57	29.04	13.67	5.24	24.56	20.00	224.9	835	843	54850
	4	11.05	28.26	13.89	5.29	24.35	20.12	224.7	849	844	55190
	5	11.21	50.03	13.37	8.47	24.12	21.28	229.1	838	821	53500
	6	11.57	51.49	13.42	8.55	25.56	21.48	229.6	844	829	57740
	7	10.89	51.23	12.88	8.57	25.36	21.30	243.1	899	766	51370
	8	11.11	56.07	13.72	8.13	25.88	21.50	242.2	819	758	52530
Summer	9	11.21	41.23	14.75	7.38	22.41	18.57	230.3	820	735	52550
	10	11.17	46.75	15.16	7.41	24.14	20.77	232.4	816	732	55290
	11	10.98	42.33	13.11	7.06	22.52	19.52	219.8	838	841	54000
	12	11.04	44.19	14.21	7.53	23.35	19.74	223.7	842	833	54880
	13	13.97	33.85	10.83	7.02	22.55	18.59	229.6	856	743	51500
	14	14.05	34.07	11.18	7.33	22.56	19.91	230.5	868	747	53360
	15	11.57	33.98	11.55	6.73	21.05	18.99	231.2	861	753	51150
	16	14.05	34.14	12.33	7.31	22.88	19.79	230.3	865	755	51390
Average ± SD		11.61 ± 1.177	32.29 ± 1.368	13.14 ± 1.199	7.026 ± 1.231	23.64 ± 1.236	20.03 ± 0.870	226.3 ± 12.30	849.5 ± 17.33	793.8 ± 49.58	53196 ± 1785

TABLE-9
AMOUNTS OF TRACE ELEMENTS DETECTED IN BLACK PEPPER SAMPLES BY FAAS
ANALYZED METAL CONTENTS [(mg kg^{-1}), n = 3]

Black pepper	No.	Co	Ni	Cr	Cu	Zn	Pb	Mn	Mg	Fe	Ca
Winter	1	11.81	32.41	10.03	4.17	29.34	20.09	208.3	544	882	61480
	2	11.96	33.61	10.55	4.32	29.97	20.19	206.7	552	875	61690
	3	11.47	31.03	10.04	3.60	29.87	19.01	203.5	535	864	61910
	4	12.62	33.16	10.21	3.90	29.99	19.31	211.9	539	857	62010
	5	11.13	33.45	10.71	3.09	29.65	18.50	154.9	492	965	64230
	6	11.23	33.69	10.83	3.23	29.00	18.33	169.9	479	962	64630
	7	11.03	39.99	10.87	3.70	29.05	20.40	211.1	582	915	67680
	8	12.19	31.84	10.74	3.87	29.06	19.05	211.9	583	929	68300
Summer	9	13.03	33.72	10.57	6.37	29.73	18.96	222.1	591	922	65860
	10	13.27	33.99	10.88	6.55	29.91	19.48	232.1	597	996	65710
	11	12.62	32.02	10.16	5.49	25.99	19.77	245.3	537	958	62160
	12	13.44	33.68	10.85	5.73	26.14	20.07	234.2	542	983	62000
	13	11.60	34.04	10.14	5.08	27.04	20.99	209.4	541	935	62800
	14	11.79	34.13	10.49	4.94	27.89	21.04	211.6	542	966	60130
	15	10.96	32.97	10.69	3.15	27.51	21.24	216.7	552	991	61710
	16	11.91	34.01	10.67	4.85	28.96	21.97	215.4	541	989	62840
Average ± SD		12.00 ± 0.720	32.98 ± 1.045	10.46 ± 0.274	4.501 ± 1.104	28.62 ± 1.310	19.90 ± 1.035	210.3 ± 22.33	546.9 ± 32.38	936.9 ± 46.08	63446 ± 2389

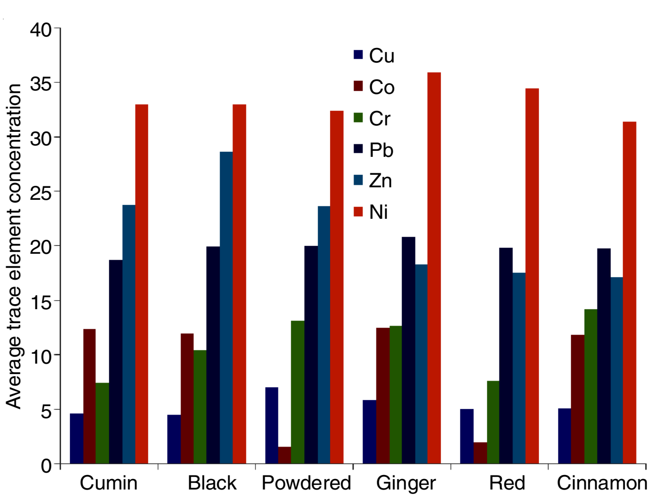

Fig. 1. Average trace element (Cu, Co, Cr, Pb, Zn, Ni) contents of spice samples (mg kg^{-1})

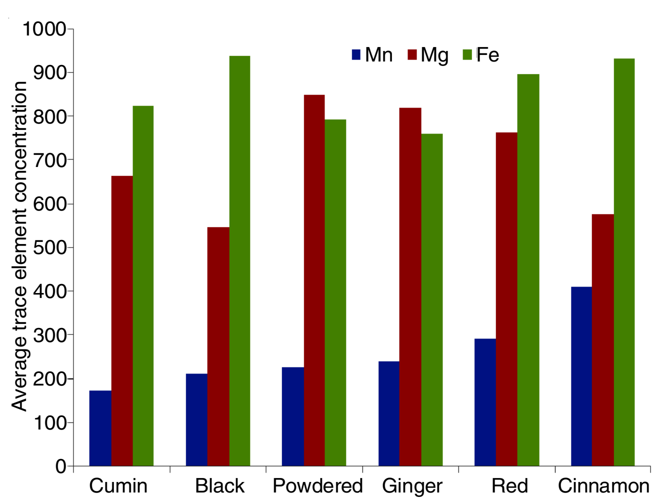

Fig. 2. Average trace element (Mn, Mg, Fe) contents of spice samples (mg kg^{-1})

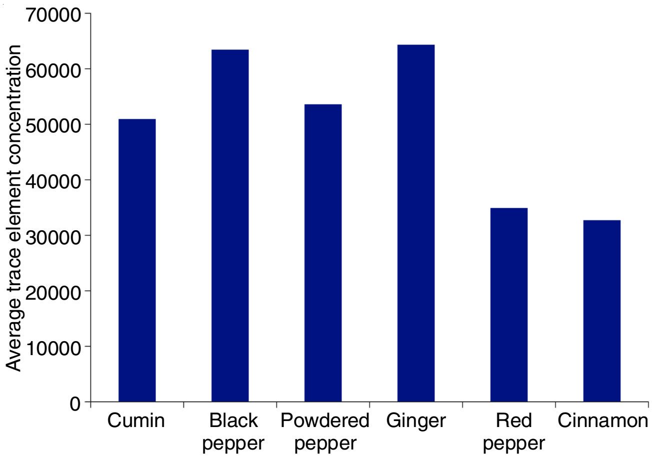

Fig. 3. Average trace element (Ca) content of spice samples (mg kg^{-1})

such as China and the Republic of Korea have identified a total toxic metal limit of 20-30 mg kg^{-1} [22].

Copper is an essential element for the functioning of many significant enzyme systems. A copper level of 2 mg L^{-1} in drinking water should not cause any adverse effects and provides an enough margin of security [23]. Copper was identified in all analyzed spice samples and was in the range of 3.09-8.57 mg kg^{-1}. The maximum Cu concentrations were found in the powdered pepper samples, no. 7 (8.57 mg kg^{-1}) and the minimum Cu concentrations were found in the black pepper samples, no. 5 (3.09 mg kg^{-1}).

The richest food sources of cobalt are green vegetables and fresh grains (0.2–0.6 mg kg^{-1} dry mass) [24]. Tobacco includes cobalt at weight, < 0.3–2.3 mg kg^{-1} dry and 0.5 % of the Co is present in main smoke [25,26]. In the present study, the highest concentration of Co was detected in the cumin samples, no. 10 (14.06 mg kg^{-1}). The average Co concentration was found in all samples in the range of 1.61–14.06 mg kg^{-1}.

Zinc is an necesssary element for human health. It has been known as a co-factor of the superoxide dismutase enzyme, which is involved in protection against oxidative processes [27]. The average concentration of Zn in spice samples were found in the range of 17.13–28.62 mg kg^{-1}. The research showed that spices are a rich source of Zn, an element which helps many enzymatic reactions in the human body. Sattar *et al.* [28] reported that the lowest and highest amounts of Zn were detected as 64.2 and 65.8 µg g^{-1} in spices and dry fruits from Pakistan, respectively. Alam *et al.* [27] reported that the average weekly intake of Zn(II) ion from Samta vegetables is estimated to be 25 mg. The maximum level of zinc ion permitted for food is 5 mg kg^{-1} by Turkish Food Codex [29]. The maximum allowable daily intake of Zn is 0.3–1.0 mg kg^{-1} [30]. Our amounts for Zn in the spice samples worked were above the WHO values.

Lead is like to be Cd, Hg, As that does not have a useful role because it produces toxicity in human metabolism. Exposure to lead is worrying due to possible harmful effects on intelligence [27]. People may be exposed to lead element through air, water and food. Lead is accumulating in bones and it can take in place of calcium. Lead constitues health problems like sleeplessness, tiredness, hear and weight loss. WHO has established a temporary permissible weekly intake for lead of 0.025 mg kg^{-1} of body weight [31]. Lead was found in all spice samples and concentrations ranged from 16.83 to 23.43 mg kg^{-1}. The WHO detected Pb concentration limit in herbal products as 10 mg kg^{-1} [32]. In the present study, all lead contents were above this limit.

According to WHO, nickel compounds are a health risk for humans. Because nickel compounds cause cancers in humans and metallic nickel is possibly carcinogenic [33]. The range of nickel concentrations in analyzed spice samples were 27.03–56.07 mg kg^{-1}. We acquired the highest content of nickel in the powdered pepper samples, no. 8.

Manganese is one of the vital significant elements. Manganese is found in the structure of some enzymes and plays an active role in some enzymes. The range of manganese concentrations in analyzed spice samples were 122.9–482.0 mg kg^{-1}. Barnes reported that the average concentration of Mn in apricot of USA, 0.273 mg kg^{-1} [34]. The levels of Mn in our samples are higher than in apricots of USA. The Institute of Medicine suggests that intake of manganese from food. The amount of Mn taken with water and diet during the day should not exceed 11 mg [35]. The US National Academy of Sciences suggested 2.5-5.0 mg per day manganese [36] and the WHO (World Health Organization) suggested 2-9 mg per day for an adult [37].

The minimum and maximum amounts of iron in spice samples were found as 702 mg kg^{-1} (red pepper, no. 5) and 991 mg kg^{-1} (black pepper, no. 15), respectively. Spice was also well resources of Fe. The concentrations of Fe in different spices, dry fruits and plant nuts commonly ingested in Pakistan were determined in the range of 142–285 µg g^{-1} [28]. Ghaedi *et al.* [38] reported that the level of Fe(III) ion was detected as 0.568 µg g^{-1} in orange juice of Iran. The amount of iron in spice samples from Turkey is higher than Fe contents in apricot of Pakistan and in orange juice of Iran. The highest iron ion level allowed for food is 15 mg kg^{-1} according to Turkish Food Codex [29]. Iron ion levels in the most of analyzed spice samples were detected to be higher than legal limits.

The average range of calcium concentration is 28490 mg kg^{-1} (cumin, no. 3) to 69630 mg kg^{-1} (ginger, no. 7). These values were found to be above the permissible normal concentration.

Looking at the Mg concentration in the 96 spice samples, the lowest value of magnesium was 492 mg kg^{-1} in the black pepper samples no. 1, whereas the highest level was 999 mg kg^{-1} in red pepper samples no. 3.

Chromium is significant for glucose toleration in human body. Chromium together with insulin facilitates the ingestion of glucose into the cells. In persons with disrupted glucose tolerance, like those with diabetes, hypoglycemia and obesity, supplementation with chromium is of exceptional importance. When the chromium diminishes, the sugar levels on the side are increased because the effect of insulin is blocked. Thus glucose can not be transported to the cell for energy production [39]. Chromium was found in all spice samples and concentrations ranged from 6.15 mg kg^{-1} (red pepper, no. 5) to 15.79 mg kg^{-1} (ginger, no. 3). Reported Cr values for apricot samples in the literature (6.43 and 3.23 mg kg^{-1}) [40] are higher than those found in the present study.

Metal pollution index: Metal pollution index (MPI) was calculated for spice samples analyzed. This calculation was done to examine all metal concentrations. Metal pollution index was obtained by calculating the geometrical mean of concentrations of all the metals in the samples with the equation:

$$\text{Metal pollution index} = (\text{Cf1} \times \text{Cf2} \ldots \text{Cfn})^{1/n}$$

where Cfn = concentration of the metal n in the sample [41].

In our study, metal pollution index ranged from 20.57 to 23.28. For calculate the metal pollution index of the spices, the average concentration amounts of the chosen metals (Ni, Co, Zn, Pb, Mn, Cu, Cr) have been taken into account. The highest metal pollution index value in the spices was observed for the powdered pepper (23.3) and the lowest for the cinnamon (20.6) (Fig. 4). The metal pollution index values of our study were found to be higher than Richeir and Gobert [42] and Richer *et al.* [43] studies.

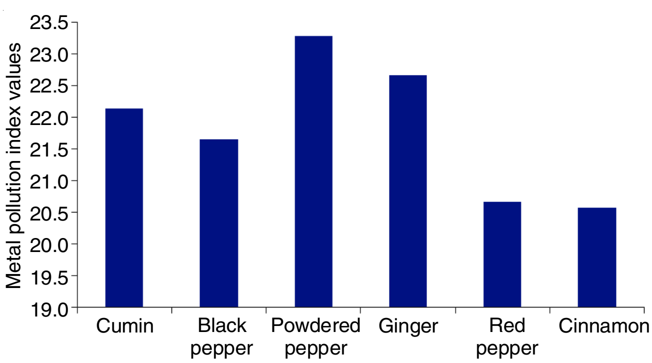

Fig. 4. Metal pollution index for spice samples (mg kg^{-1})

Conclusion

In this study, the analytical approach to the research of ten trace metals in the spice samples. In addition, each sample was analyzed by FAAS to detect heavy metal ingredients. Ninety-six spice samples, collected from market places in Karaman, Turkey, were determined by using FAAS after wet burning method. FAAS determines quantities of trace elements in plants. Local, spices are in general a well dietary source, particularly in macro and micro-nutrients. It is thought that the sources of the trace elements in the spices are caused by soil, fertilizer, water or environmental metal pollution. Furthermore, in terms of plant features, differences in the geographic area, genetics and compound of the soil can influence the level of trace metals. In present case, trace element contents in the analyzed samples were probably to be of remissible anxiety. The concentrations of minor and trace elements were mostly variable, largely dependent upon the type of spices analyzed, in accordance to the published literatures. Each spice was found to be the rich source of at least one or more nutritionally essential trace elements (Zn, Cu Cr) or probable essential trace elements (Mn, Ni, Co) specified by WHO. The levels of toxic heavy metals were in accordance to the published literatures around the world on spices and within the critical limits specified by FAO/WHO, Food and Nutrition Board, Turkish Food Codex. Especially in the spices analyzed, the presence of toxic trace elements such as Cr, Pb, Ni and Fe may have a high contribution to total metal uptake. This situation could pose a threat to the consuming population. Cu, Zn, Co, Mg, Ca and Mn TGK was found to be within the permissible limits [44].

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