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Concentration of selected heavy metals in spices, dry fruits and plant nuts

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Abstract. Different spices, dry fruits and plant nuts commonly consumed in Pakistan were assayed for the heavy metals cadmium, lead, copper, zinc, iron and manganese by the potentiometric stripping analysis and AA spectrophotometry. The results revealed wide variation in heavy metal content among different biological materials. Mixed spices generally exhibited higher value for trace metals specially lead (6.6–9.2 μg/g), cadmium (0.65–1.34 μg/g), iron (142.3–285.0 μg/g) and zinc (64.2–65.8 μg/g). Dry fruits contained relatively lesser amounts of heavy metals than plant nuts. Almonds contained higher levels of lead (1.02 μg/g) and cadmium (0.24 μg/g) than other nuts and dry fruits.

Introduction

Spices are dried products of plants which have been used since long as diet components often to improve aroma, palatability and acceptability of food [23]. They consist of rhizomes, barks, leaves, fruits, seeds and other parts of plant. Most of these are fragrant, aromatic and pungent. The bulk of the dry matter of these products consists of carbohydrates, organic compounds of carbon, hydrogen and oxygen. Dry fruits and plant nuts are considered a major source of income and foreign exchange in many countries and are widely consumed around the world during all seasons [8]. Essential and toxic trace elements are present in low concentrations in these food materials depending upon their production sites. Monitoring of trace metals in biological materials has gained importance in recent years either due to their role in controlling some of the vital biological processes or their potent toxicity for living organisms [15]. Heavy metals can be determined by several techniques such as neutron activation analysis, atomic absorption (AA) spectroscopy, anodic stripping voltammetry and potentiometric stripping analysis [3, 11, 19, 24]. Potentiometric stripping analysis (PSA) is an electrochemical approach for the assay of trace metals [10]. It appears to be widely applicable as stripping voltammetry and differential pulse stripping voltammetry [12, 13]. Moreover, the resolution of the technique compares well with that of the differential pulse voltammetry [27]. Stripping analysis, potentiometric as well as voltammetry are particularly well suited in liquid samples since normally no pretreatment of such samples is necessary. Although levels of selected heavy metals in some biological materials of undefined origin have been determined [9, 21], their concentration in materials especially spices, plant nuts and dry fruits widely consumed in this and other countries, is not available. The objective of this work was to determine the levels of the heavy metals cadmium, copper, lead, zinc and manganese and iron in commonly consumed biological materials.

Materials and methods

The samples of different spices, dry fruits and plant nuts were obtained from a wholesale agency in Peshawar, which imports/collects and then distribute throughout Pakistan. They were sorted, cleaned, and dried in an oven. The dried material was ground to pass through 40 mesh in Wiley mill and kept in plastic bottles for further analysis. There was one sample, analyzed in triplicate, of each material.

Moisture was determined by drying the samples at 105 °C in an oven. For heavy metal assays, wet digestion of the samples was done using the method of O'Dell et al. [19] modified for macro levels [26]. Simultaneous determination of cadmium, copper, lead and zinc was carried out in the acid digest by the potentiometric stripping technique [2] using the Tecator Striptec system comprising glassy carbon electrode, saturated calomel electrode (SCE) and platinum wires as counter electrode. The stripping curves were measured at potential -1.1 volt vs SCE and 180 second plating time for cadmium, copper and lead while -1.3 volt vs SCE and 180 second plating time for zinc. The concentration of the metals in the samples was evaluated by means of the standard addition technique; the 1-min pre-electrolysis/stripping cycle being repeated after each addition. In comparison to calibration curves, the standard addition method is considered to be appropriate especially when the samples are of varying type and origin. In most experiments, two standard additions were used and the concentration of the standard addition solution was chosen so that the first addition almost doubled the concentration of the analyte. The stripping time for the element considered was prolonged in proportion to the added amount. Then the unknown content in the acid digest and finally the sample was determined by simple calculations. Details of the methodology are available elsewhere

[9, 13]. The assays for manganese and iron were made by the atomic absorption spectrophotometry using Hitachi model 170-10 atomic absorption spectrophotometer.

Results and discussion

Moisture and heavy metal contents of different spices are presented in Table 1. The precision of the two analytical techniques was earlier determined by analysing the same digest five times, and was of the order of $\pm 10\%$. This was considered satisfactory in the concentration ranged under consideration. The accuracy of this method has been demonstrated already [2]. The moisture levels in spices varied from 2.90 to 14.83%; the highest was in the ginger and least in the parsley. Most of the samples had the water content between 5 and 11%. Ginger is invariably consumed in the semi-dried form and therefore, contained relatively higher moisture. The water levels encountered in these spices indicate less possibility of fungal contamination and propagation.

Mixed spices (Sultani) contained highest level of cadmium while the onion powder the lowest. The cadmium content of various other spices varied from 0.09 to 0.66 μg/g. The amount of lead in the samples ranged 0.02–9.2 μg/g. Mixed spices (National) were found to have maximum lead followed by mixed spices (Sultani). Turmeric, chillies, black pepper, caraway, coriander and cinnamon also had considerable amounts of lead. The maximum amount of copper was in black pepper (21.5 μg/g), followed by mixed spices (20.5 μg/g), cumin (8.7 μg/g), turmeric (17.2 μg/g) and coriander (14.0 μg/g). Other spices contained 2.9–13.9 μg/g copper. The lowest amount of copper was in onion. The concentration of zinc varied between 12.6 and 65.8 μg/g. Mixed spices (Sultani), cloves, black pepper, caraway, cumin and cardamon generally had higher amounts of zinc than other spices. The highest level of iron was found in caraway (300 μg/g) followed by mixed spices (Sultani) i.e. 285 μg/g, cumin (248 μg/g), turmeric (219 μg/g) and parsley (150 μg/g).

Ginger was rich in manganese, 97 μg/g, while in other samples it ranged from 12 to 95 μg/g. The spices were relatively higher in iron and low in cadmium contents. However considerable variation was found among various spices. Waldraw and Stofen [28] reported that lead concentration in food products ranged from undetectable levels to a few mg/kg of wet weight. The range of natural concentration of lead in food was 0.01–2.5 mg/kg depending on types of food [5]. Studies performed at other places [12, 13, 29] indicated that most of food stuffs had cadmium concentration in the range

Table 1. Moisture and heavy metal contents of spices.

Spices	Moisture (%)	Cadmium (μg)	Lead (μg)	Copper (μg)	Zinc (μg)	Iron (μg)	Manganese (μg)
Cinnamon	11.22 ± 0.98	0.35 ± 0.10	3.55 ± 0.50	5.20 ± 0.77	13.4 ± 1.55	46.80 ± 2.60	63.75 ± 2.19
Ginger	14.83 ± 0.75	0.44 ± 0.02	1.27 ± 0.20	12.00 ± 2.83	25.2 ± 3.90	38.60 ± 1.24	97.20 ± 1.97
Cardamon (small)	5.82 ± 0.35	0.22 ± 0.03	0.98 ± 0.01	13.87 ± 2.25	27.5 ± 2.10	58.81 ± 0.99	95.0 ± 1.81
Cardomon (large)	9.66 ± 0.42	0.64 ± 0.04	1.70 ± 0.29	10.96 ± 1.55	30.2 ± 1.77	48.01 ± 2.83	58.00 ± 2.83
Coriander	11.43 ± 1.20	0.61 ± 0.02	3.40 ± 1.40	14.00 ± 2.00	32.3 ± 1.13	120.00 ± 2.55	20.35 ± 3.00
Cumin	7.85 ± 0.56	0.18 ± 0.02	1.35 ± 0.21	18.72 ± 2.96	38.95 ± 0.35	247.81 ± 1.27	29.00 ± 1.55
Caraway	6.55 ± 0.35	0.53 ± 0.40	5.41 ± 0.28	12.91 ± 1.55	49.5 ± 0.70	300.15 ± 1.90	38.82 ± 2.96
Parsley	2.90 ± 0.05	0.48 ± 0.03	0.75 ± 0.09	8.35 ± 1.20	35.80 ± 3.50	150.00 ± 2.19	25.70 ± 1.27
Black pepper	9.26 ± 0.35	0.49 ± 0.04	3.80 ± 0.28	21.51 ± 1.25	36.9 ± 4.40	138.70 ± 1.60	47.65 ± 1.20
Chilli	8.34 ± 0.42	0.45 ± 0.03	4.91 ± 1.41	5.90 ± 0.99	16.7 ± 0.42	53.25 ± 2.00	12.12 ± 0.49
Onion	7.88 ± 0.89	0.015 ± 0.007	0.02 ± 0.007	2.89 ± 0.91	12.65 ± 1.20	10.20 ± 0.98	12.90 ± 0.89
Garlic	7.38 ± 0.98	0.22 ± 0.03	0.28 ± 0.03	7.21 ± 0.99	13.7 ± 1.13	105.00 ± 1.90	8.65 ± 1.20
Clove	5.67 ± 0.35	0.09 ± 0.004	0.76 ± 0.07	6.60 ± 0.56	35.5 ± 1.41	51.00 ± 1.76	89.90 ± 0.42
Turmeric	5.80 ± 0.56	0.66 ± 0.11	6.40 ± 0.42	17.20 ± 1.10	23.2 ± 1.60	218.70 ± 2.70	35.10 ± 1.42
Mixed spices (National)	10.60 ± 0.90	0.65 ± 0.07	9.20 ± 1.10	12.30 ± 1.69	64.2 ± 2.20	141.30 ± 1.90	38.10 ± 0.70
Mixed spices (Sultani)	10.82 ± 0.35	1.34 ± 0.03	6.60 ± 0.56	20.50 ± 1.41	65.8 ± 1.28	285.00 ± 1.41	43.50 ± 0.50

Values refer to dry weight of samples; the standard deviations quoted refer to 3 measurements.

of 0.005–0.1 μg/g depending upon the type and places of production. These values have been obtained in areas generally believed to be uncontaminated by cadmium. Lead is generally known to persist on materials even at large distances from the road as a consequence of the transport of aerosol matter whereas cadmium pollution is an environmental concern only for leafy crops in close proximity to the edge of a road [16]. Wolnick et al. [29] analysed the raw agricultural crops collected from major US growing areas uncontaminated by human activities other than normal agricultural practices and found a mean cadmium and lead concentration of 0.11 and 0.17 μg/g in onions and tomatoes on wet weight respectively. These results were generally comparable with our investigation and it was noted that overall cadmium concentration was considerably lower in all the investigated spices. Schroeder [25] reported that various spices contained on the average, 23 μg/g of zinc and 6.8 μg/g of copper. The data for essential trace metals were comparable to those reported by other workers [1, 6, 17]. The determination of CV showed highest variation in lead followed by cadmium, zinc, copper and moisture contents for various spices used in the study.

Since dry fruits and plant nuts form a major portion of the daily diet for the population in northern parts of Pakistan, these were also assayed for moisture and heavy metal contents. From the results presented in Table 2, it was observed that moisture values varied between 2.6 and 24.5% and the level was generally higher in dry fruits than dry nuts.

The concentration of lead was highest in almond (1.0 μg/g) followed by groundnut (0.49 μg/g), pinenut (0.43 μg/g), apricot (0.32 μg/g) and others. The lowest amount of lead was in dry dates (0.12 μg/g). The amount of copper in dry nuts was found between 2.6 and 25.5 μg/g. The maximum amount was in apricot followed by date, raisin and other dry fruits and nuts. Dry nuts relatively contained lower amounts of copper than dry fruits. The concentration of cadmium was found to vary between 0.20 and 0.25 μg/g. Almond was highest in cadmium while raisin contained lower amounts of this element. The values of zinc in these dry fruits and nuts ranged 1.7–22.9 μg/g. The maximum amount was in almond and least in the raisin. It was also interesting to find that plant nuts contained comparatively higher levels of zinc than dry fruits. The overall results revealed higher amounts of lead, cadmium and zinc in almond than other fruits and nuts. The measurement of CV indicated wide differences in heavy metal content of the samples. In a recent report, Preer and Rosen [21] reported higher levels of heavy metals in some vegetables from urban gardens than those grown in rural areas due to greater contamination of urban soil and air than rural areas. Jelinek [14] reported lead content of fresh potatoes, cabbages, onion, carrot

Table 2. Moisture and heavy metal contents of dry fruits and nuts

Dry fruits and nuts	Moisture (%)	Cadmium (μg)	Lead (μg)	Copper (μg)	Zinc (μg)	Iron (μg)	Manganese (μg)
Almond	4.80 ± 0.21	0.24 ± 0.04	1.02 ± 0.05	6.20 ± 0.66	22.90 ± 1.78	44.30 ± 3.45	21.30 ± 1.70
Walnut	3.65 ± 0.49	0.113 ± 0.01	0.19 ± 0.035	7.74 ± 0.84	22.22 ± 0.26	29.30 ± 2.10	18.20 ± 1.77
Pinenut	3.29 ± 0.08	0.12 ± 0.01	0.43 ± 0.02	3.93 ± 0.61	8.78 ± 0.83	12.71 ± 0.90	5.92 ± 0.71
Groundnut	2.60 ± 0.50	0.09 ± 0.01	0.49 ± 0.04	2.6 ± 0.07	19.77 ± 2.65	17.62 ± 1.76	6.31 ± 0.74
Date	20.19 ± 0.67	0.08 ± 0.01	0.12 ± 0.028	18.0 ± 2.83	3.90 ± 0.42	19.00 ± 1.88	2.14 ± 0.16
Apricot	24.19 ± 1.55	0.10 ± 0.01	0.32 ± 0.04	25.0 ± 1.41	4.80 ± 0.28	45.00 ± 3.67	17.23 ± 1.00
Raisin	24.50 ± 2.12	0.02 ± 0.001	0.19 ± 0.03	14.90 ± 1.55	1.70 ± 0.14	33.64 ± 2.60	8.55 ± 0.56
Fig	24.17 ± 1.77	0.09 ± 0.001	0.20 ± 0.03	3.90 ± 0.42	4.9 ± 0.36	32.33 ± 1.88	4.92 ± 0.41

Values refer to dry weight of samples; the standard deviations quoted refer to 3 measurements.

and tomatoes, as 0.05, 0.04, 0.18, 0.14, 0.08 μg/g in fresh and in 0.12, 0.08, 0.32, 0.13, 0.30 μg/g in canned packs respectively, which were comparable with the values found in present work.

From this study it can be concluded that the spices and dry fruits and plant nuts widely vary in their essential and toxic metal contents. On the basis of dietary consumption pattern in different sections of the society in Pakistan, the mean essential elemental contents would meet the recommended daily requirements [4] only of a very small portion of the population. The people living in northern areas adjoining China, Afghanistan and USSR who are famous for longevity are receiving more than sufficient levels of essential metals. The joint FAO/WHO Expert Committee [3] had set tolerable weekly intake limits for lead and cadmium as 3 mg and 315–330 μg respectively per person. Reliable base line data for heavy metals are not available in developing countries. The background values are needed for evaluating the toxicological and nutritional significance of consumption of these elements and their possible increase due to local food processing methods.

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