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ESTIMATION OF CERTAIN TOXIC TRACE METALS IN VARIOUS LOCAL FOOD COMMODITIES BY ATOMIC ABSORPTION METHOD

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Employing standard analytical methods and the atomic absorption technique, toxic trace metal residues are estimated in 103 food samples. The samples, belonging to the broad classes of grains and cereals, spices and condiments and fruits and vegetables, were collected from the Punjab, NWFP, Baluchistan and Azad Kashmir areas. The data pertain to the estimation of lead, cadmium, nickel, mercury and arsenic. Percent recoveries are reported to validate applicability of the analytical methods used to this effect. The overall precision in individual estimation was better than ± 1.6 percent. The reported results appear at 2S confidence level for at least five replicate measurements.

Key words: Toxic trace metal analysis; Food analysis and trace metal estimation.

INTRODUCTION

In recent years, the role of trace elements in food both in nutrition and toxicological interest has been recognised. Monitoring of the background levels of trace metals is carried out in many countries to keep a constant check on their national food supply. Although it is difficult to classify trace metals into nutritious and toxic groups, yet it is well known that the nutritious (or essential) metals become toxic at sufficiently high intakes and the margin between levels that are beneficial and those that are harmful may be small. Increasing industrialization, motorization, burning of fossil fuels, have all greatly polluted the invironment with several toxic trace elements [1]. Higher concentrations of several hazardous trace metals such as lead, cadmium, nickel, mercury and arsenic have been found in various foodstuffs analysed as to their metal contents all over the world [2]. The situation has obviously caused deep concern to the relevant public health authorities. Little is yet known of the maximum safe limits due to long term exposure of man to most of these elements through food, water and air. The matter becomes more complicated in view of the fact that the health impact of individual trace elements cannot be considered in isolation from other aspects of man's dietary intakes. These toxic elements frequently interact with each other and with the essential trace elements at the absorptive and tissue level which makes the work more difficult for laying a single minimum or single maximum intake standard. An excellent account of the limiting levels appears in a WHO technical report [3].

Consequently, from the viewpoint of the study of metabolism, toxicity, exposure effects and short/long term health based exposure limits, the analysis of foods for trace metals is rather inevitable. Also, biological limits of these metals in respect of their carcinogenic, mutagenic and teratogenic effects have yet to be defined. Trace metal study in foods appears to be incomplete, both in terms of health hazards and nutritional values, unless chemical forms in which heavy metals exist in foods are characterized. This would warrant a deeper understanding of the variation of toxicity of metals between their inorganic and organic counterparts.

In line with these objectives, an attempt has been made through the present study to determine the levels of residues of lead, cadmium, nickel, mercury and arsenic present in various commodities of Pakistani raw foods including grains and cereals, spices and condiments, fruits and vegetables. In all, 103 food samples have been analysed using the atomic absorption technique, coupled with the standard methods of estimation recommended by WHO, for the estimation of lead, cadmium, nickel, mercury and arsenic contents in these food groups.

MATERIALS AND METHODS

Food samples were collected through Government agencies at the division and district levels of the provinces

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of the Punjab, Sind, NWFP and Baluchistan. The main commodities received consisted of raw grain and cereals, pulses, condiments and spices belonging to arid, semiarid and developed lands. As soon as the samples were received they were cleaned of any foreign matter and impurities and then ground in a ball-mill into a coarse powder of uniform particle size. After preparation, the samples were coded and deep freezed till the time of analysis. The food samples screened for the residues of lead, cadmium, nickel mercury and arsenic are shown in Table 1. The analytical methodology adopted for determining trace elements in this study essentially consisted of two steps [4] : (1) sample preparation which includes the destruction of organic matrix by dry ashing or wet-ashing; and (2) estimation of trace metal level by the atomic absorption method. While the relative results of dry-ashing and wet-ashing for destroying organic matrix prior to determining trace elements might vary, the technique employed in trace analysis during this work is strictly based on internationally recommended WHO procedures [5]. The mercury was estimated as per AOAC method, and lead and cadmium were estimated through WHO method. The arsenic analyzer unit was used for the estimation of arsenic through the atomic absorption of arsine generated from the reduction of the sample solution. Direct aspirations were conducted for nickel.

Reference standards were obtained from FAO. The reagents and solvents were tested as blanks to avoid any possible quantitative errors in metal analysis. Deionized water was used throughout this work.

Optimum working conditions for atomic absorption were achieved in terms of air and fuel flow rates, lamp current, and burner height for each metal separately. All measurements were made at 0.4 nm band pass at specific wave length for a given metal on a Hitachi atomic absorption spectrophotometer. The quantification was done by the standard curve technique. For consistency check, spiked recovery experiments were performed on variety of samples throughout the study in addition to reagent blank tests.

RESULTS AND DISCUSSION

In Table 1 are listed groups of food commodities analysed for various trace metals. The results of analyses are shown in Table 2. A summary of recovery data appears in Table 3.

Analytical results of wheat samples collected from different geographical areas of Pakistan show that the highest level of lead is present in wheat-200 received from Multan. Similarly, maximum cadmium was detected in wheat-100, received from Rawalpindi. Wheat-3000 showed maximum nickel content. This sample was received from Sukkur. Mercury occured at maximum level in wheat 2000 received from Lahore. Arsenic was detected at maximum level in wheat 400 received from Malakand.

Maximum level of lead residue was found in rice sample 300, received from Peshawar, while the correspon-

Table 1. Food commodities collected from different areas of Pakistan.

S. . No.	Commodity/Code	No. of samples	Source
	GRAINS AND CERALS		
1.	Wheat 100-3000	13	Punjab, Sind, NWFP, Baluchistan, Azad Kashmir
2.	Rice 200-4000	15	– do –
3.	Maize 100-4000	13	– do –
4.	Pulses gram 100-4000	11	Punjab, Sind, NWFP, Baluchistan
5.	Mash (Black gram) 100-4000	11	– do –
6.	Mong (Green gram) 100-5000	12	– do –
7.	Masur (lentil) 100-4000	12	– do –
	SPICES AND CONDIMENTS		
1.	Coriander 200, 6000, 900, 1000, 5000	5	Multan, D. G. Khan, Bahawalpur, Sargodha, Kalat.
2.	Turmeric 100-200	2	Rawalpindi, Multan

Table 2. Range of concentrations of metallic residues found in different food commodities (mg/kg).

		No. of	Lead			Cadmium			Nickel			Mercury			Arsenic		
S. No.	Commodity	Samples	Min.	M.P.**	Max.	Min.	M.P.	Max.	Min.	M.P.	Max.	Min.	M.P.	Max.	Min.	M.P.	Max.
1.	Wheat	13	0.07	1.20	1.65	0.11	0.18	0.25	0.61	2.00	2.37	*	*	0.07	0.04	0.10	0.21
2.	Rice	15	0.29	0.71	0.90	0.04	0.11	0.18	0.31	1.12	1.63	0.02	0.11	0.17	0.11	0.13	0.21
3.	Maize	13	0.43	0.81	1.24	0.06	0.09	0.16	0.49	2.87	3.78	0.01	0.03	0.07	0.10	0.11	0.21
4.	Pulses gram	11	0.79	1.23	1.51	0.08	0.16	0.32	0.59	3.49	5.36	*	0.04	0.08	*	0.20	0.24
5.	Mash (Black)	11	1.13	3.11	3.83	0.10	0.14	0.18	1.58	4.00	5.66	0.04	0.03	0.05	*	0.10	0.16
6.	Mong (Green gram)	12	0.72	0.93	1.57	0.09	0.13	0.17	0.99	2.87	3.46	0.01	0.02	0.04	*	0.03	0.09
7.	Masur (lentil)	12	0.60	1.83	2.14	0.09	0.12	0.17	0.99	4.31	6.11	*	0.41	0.63	*	0.09	0.19
8.	Coriander	5	2.41	2.71	3.38	0.14	0.19	0.23	2.76	3.21	5.64	*	0.11	0.16	0.20	0.13	0.21
9.	Turmeric	2	23.17	35.20	43.48	0.19	0.13	0.21	1.13	1.00	1.62	*	0.02	0.03	0.11	0.10	0.20
10.	Vegetables and fruits	9	0.57	1.92	3.27	0.01	0.03	0.07	0.12	0.21	0.38	*	0.01	0.02	–	–	–

– not detected; *below detection; **most probable levels based on frequency distribution.

Table 3. Recovery data on metallic residues found in various foods.

S. No.	Food	Lead % Recovery	Cadmium % Recovery	Nickel % Recovery	Mercury % Recovery
1.	Rice	81.3	97.2	83.2	89.7
2.	Pulses gram	82.6	95.0	84.9	91.2
3.	Wheat	86.1	85.6	83.0	95.6
4.	Masur (lentils)	76.7	94.5	86.7	85.3
5.	Mash (Black gram)	69.8	83.8	92.2	89.2
6.	Turmeric	81.8	73.4	78.5	80.0
7.	Tomatoes	88.0	89.0	95.1	98.4
8.	Oranges	81.8	84.0	94.4	93.7

ding maximum levels for other metals were: cadmium in rice-400, Malakand; nickel in rice-3000, Peshawar; mercury in rice-800, received from Hyderabad and arsenic in rice-600, Dera Ismail Khan.

In the case of maize, the highest residual lead was found in maize 200, received from Multan; cadmium in maize 300, received from Peshawar; nickel in maize 500, received from Hazara; and mercury and arsenic in maize samples belonging to the Punjab.

Data on samples of pulses gram pertaining to various trace metals indicate that lead occurred at highest level in pulses gram 100, received from Rawalpindi, cadmium in pulses gram 200, received from Lahore; nickel in pulses gram 300 from Sukkar; mercury in pulses gram 200 from Multan and arsenic in pulses gram 1000, received from Sargodha. Mash 3000 sample received from Sukkar showed the highest level of lead while that of cadmium was found in mash 400, received from Malakand. Nickel was maximum in mash 500, received from Hazara.

In the case of mong, the following situation emerged in respect of highest level of trace metals; lead in mong 400, received from Malakand; cadmium in mong 100, received from Rawalpindi; nickel in mong 1000, received from Sargodha; and arsenic in mong 800, received from Hyderabad.

The highest concentration in the case of lead was found in masur 500, received from Hazara, cadmium in masur 1000, received from Sargodha; nickel in masur 700, received from Karachi; mercury in masur 4000, received from Azad Kashmir and arsenic in masur 1000, received from Sargodha.

As regards the distribution of metallic residues in vegetables and fruits in was observed that tomatoes, oranges and onion contain mercury at only few ng/kg level. The highest concentration of lead was found in spinach, and mercury in potatoes.

Results of the analysis of condiments and spices show that mercury occurred at trace metal (few ng/kg) in the case of turmeric 200, coriander 900 and coriander 200. The highest content of lead was found in turmeric 200, received from Multan, cadmium in coriander 1000 received from Sargodha.

The foodstuffs under investigation show 100% frequency of occurrence in the case of lead, cadmium and nickel. Mercury too is present at 100% level except in a few cases where minimum concentration is observed at trace levels only.

A commodity-wise study shows that the highest of lead content occurred in turmeric. A relatively lower level was found in mash (black gram) at 3.83 mg/kg. Maximum levels of lead in coriander and vegetables and fruits were close to each other. Among grains and cereals, masur (lentil) showed the maximum level of lead. The lead level in rice was 0.90 mg/kg. Wheat grain showed a maximum level of lead at 1.65 mg/kg.

The maximum limit of lead prescribed in the Food Laws [6,7] for all kinds of food and the tolerable limit quoted by the PCSIR Laboratories[8], for lead is 8.0 mg/kg. The findings for lead residue in foods as per present study remained within the stipulated tolerance limits. However, the level of lead in turmeric samples exceeds permissible limit. The highest concentration of cadmium is found in pulses gram. In descending order of concentration wheat, coriander, and rice were prominent, while mash, maize, mong and masur remained within an identical range. The lowest level of cadmium was detected in the vegetable and fruit group, while the highest was found in coriander. The permissible limit laid down in the food laws for cadmium is 0.6 mg/kg [9]. Accordingly, all food commodities were found to be within permissible limits.

The highest level of nickel occurred in masur (lentil). Coriander, mash and pulses gram showed almost same level: maize and mong had a close range of concentrations while the lowest values were encountered in vegetables and fruits. Thus, these samples show nickel content well within the permissible level [10].

The highest level of mercury was detected in masur (lentil). Coriander and rice showed an identical range of mercury while the lowest level was detected in vegetables and fruits group.

The highest concentration of arsenic occurred in pulses gram. Samples of wheat, rice, maize, masur, coriander and turmeric showed almost uniform maximum level of about 0.20 mg/kg. The lowest concentration detected was in wheat. Both arsenic and mercury levels are within the permissible levels [11,12].

A few cases have been reported where metallic mercury had been used by certain farmers as a fungicide in order to preserve wheat, rice and coriander. High mercury content in these samples might have originated from this source.

Studies on the recoveries of all the trace metals of interest were conducted as a routine matter along with the analysis of food samples. Recovery data appear in Table 3. Arsenic recoveries were not included because of the fact that small increments added at spiked levels did not show linear absorption vs. concentration relationship.

An overall view of the levels of these metallic contaminants in various commodities of food under study indicates that, in all probability, their concentrations remain well within the recommended standards laid down by the joint FAO/WHO Commission [12]. In conclusion it might be said that the levels of metallic residues of lead, cadmium, nickel, mercury and arsenic, as established in the present study, define the status of Pakistani foods in respect of metallic contaminants to be 'non-critical'. The metallic contaminants whether within or beyond recommended levels are abundantly prevalent in Pakistani agricultural products in varying levels subject to geographical regions. The observed difference in levels of trace metals in various foods may be considered to arise from the use of artificial fertilizers, plant enrichers and fungicides/pesticides etc. The present study shows that metal contamination is pronounced in the Punjab areas falling in close proximity to industrial sites, where both effluents and surface runoff affect the metal content of food. Regular monitoring for further assessment as to ascertaining the quality of these foodstuffs and the origin of trace metal distribution is a pre-requisite to this effect.

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