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DETERMINATION OF LEAD AND CADMIUM IN PULSES AND CEREALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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In the present investigation the lead and cadmium concentrations were determined in different varieties of pulses and cereals by electrothermal atomic absorption spectrophotometric technique. Milling of cereals increased the concentration of these elements in flour samples as compared to the respective grains. Pulses contained higher concentration of lead (average 452 ng g^{-1}) than that of cereals (wheat, rice, corn) (average 236 ng g^{-1}) whereas the cadmium concentration was higher in cereals (average 75 ng g^{-1}) as compared to pulses (average 17 ng g^{-1}). In cereals rice contained higher concentration of lead. The results obtained from the present study were compared with the reported values from other countries. Intake of lead and cadmium through pulses and cereals was calculated and was found to be below the recommended tolerance levels of WHO.

Key words: Lead, Cadmium, Electrothermal atomic absorption spectrophotomerty, Pulses, Cereals, Daily intake.

Introduction

Lead (Pb) and cadmium (Cd) are among the most toxic elements of primary importance in ecotoxicology. The presence of these metals even at trace levels in water, air and food may pose health hazards to human life, due to the possibility of long term exposure and their accumulation in the body with age. The harmful effects of Pb and Cd have been well documented [1-3]. Due to rapid industrialization, input of these elements into the atmosphere has increased significantly. From the atmosphere these elements find their way into human through different food chain systems. It is, therefore, necessary to monitor the levels of Pb and Cd in food articles which are the major source of intake of essential and toxic elements. Such studies will be helpful to assess the safety of human diet. Due to traditional food habits and economical considerations the people of this area consume significant quantity of pulses, wheat and rice which constitute a major part (70-80%) of food consumed particularly by middle and low income groups. The data on the levels of Pb and Cd in pulses is not available for this area. It is therefore, important to determine the concentrations of Pb and Cd in different types of pulses and cereals in order to establish a baseline level of these elements and to estimate their daily intake through this source.

Usually the concentrations of Pb and Cd in cereals are very low therefore, for such measurements, very sensitive, accurate and reliable analytical method is required. Concentration of lead and cadmium in cereals has been reported by various authors using different decomposition/ mineralization methods and analytical techniques [4-7]. Among various analytical techniques electrothermal atomic absorption spectrophotometry (ETAAS) is one of the preferred technique due to its rapidness, high sensitivity and specificity. In the present work ETAAS was used for the analysis of lead and cadmium in different varieties of pulses and cereals. This study is a continuation of our work on the measurement of essential and toxic trace elements in food items [8-11].

Experimental

Instrument. The ETAAS analyses were performed with an atomic absorption spectrophotometer of Hitachi, Japan, Model Z-8000 with zeeman effect background correction and equipped with a graphite furnace, a microprocessor and built in printer. Hollow cathode lamps of lead and cadmium were used as radiation source. Argon was used as an inert purging gas and its flow was interrupted during atomization step. The optimized heating programmes used for the determination of lead and cadmium are given in Table 1. Sample injection was done automatically using an autosampler with a precision of ± 0.1 µl. Signal evaluation was based exclusively on integrated absorbance value.

Reagents. Stock solutions (1000 mg l^{-1}) of cadmium and lead were prepared by dissolving appropriate amounts of cadmium chloride monohydrate ($CdCl_2.H_2O$) from BDH and lead nitrate $Pb(NO_3)_2$ from E. Merck in distilled deionized water. Stock and standard solutions were made in 0.02N HNO_3. Distilled deionized water was used throughout this work. Glassware was cleaned by overnight soaking in nitric acid (1+1) followed by multiple rinses with water. Analytical reagent grade perchloric acid (70%) and distilled nitric acid [12] were used for digestion of the samples.

Sampling and samples preparation. Samples of pulses and other food commodities were randomly purchased from different shops of Rawalpindi and Islamabad during

April-Sept, 1987. Samples of pulses, grams, rice wheat and maize were washed with water and were oven dried at 60°. Twenty five grams of the three samples of the same variety were taken and pulverised in a grinder with teflon coated blades and the powdered samples were further dried at 70° to constant weight. Dried powdered samples were thoroughly mixed to obtain a homogeneous sample. Homogenity of the samples was checked by analysing Zn and Cu contents by taking 0.5 g. of sample in triplicate. The variation around the mean values were found to be 6.1 and 6.4% for Zn and Cu respectively. The powdered samples were stored in bottles and were refrigerated until required for analysis.

Procedure. About 500 mg sample was taken in triplicate in 100 ml flask fitted with an air condensor of 30 cm length, and 5 ml nitric acid was added to each. This mixture was heated at 50° for 45 min. After cooling 2 ml perchloric acid was added and heated again at 280° with occassional shaking till white fumes evolved. The clear solution obtained after digestion was cooled and transferred quantitatively into a 25 ml measuring flask and the volume was made up with water. A blank was prepared similarly under identical conditions. The absorption of the standard and sample solution was measured by injecting 10 μl solution into the graphite tube of the electrothermal analyser and using the furnace programme given in Table 1. A minimum of five injections were made for each solution and the mean value of the absorption signal was used for subsequent calculations. The absorption signals of the samples were evaluated after subtracting the mean value of the blank.

Results and Discussion

Different varieties of pulses and cereals were analysed for their lead and cadmium contents. The precision and accuracy of the procedure used were checked by analysing the NBS Standard Reference Materials wheat flour (SRM-1567)

TABLE 1. CONDITIONS EMPLOYED FOR ETAAS MEASUREMENTS OF LEAD AND CADMIUM.

Analytical conditions	Lead	Cadmium
Lamp current (mA)	7.5	7.5
Wave length (nm)	283.3	228.8
Slit width (nm)	1.3	1.3
Carrier gas flow (ml/min)	100	100
Sample volume (μl)	10	10
Heating programme for Graphite furnace:		
Drying Temp°C	80-120	80-120
Time Sec.	30	30
Ashing Temp°C	400	300
Time Sec.	30	30
Atomization Temp°C	2100	1700
Time Sec.	7	7
Cleaning Temp°C	3000	2600
Time Sec.	3	3

rice flour (SRM-1568) and orchard leaves (SRM-1571) for Pb and Cd contents. Table 2 shows the comparison of measured values with the certified values, which are in good agreement.

The concentrations of Pb and Cd determined in various types of pulses namely gram, mong, mash, lentil, beans and cereals (rice, wheat and corn) are given in Tables 3 and 4. Five samples were analysed for each type of pulses and cereals and the amounts were calculated on dry weight basis.

The concentration of Pb and Cd in different types of pulses (P_1-P_{11}) range from 215-799 (average 452, median 421) and 2.0-39.0 (Average 17.1, median 13.7) ng g^{-1} respectively. The maximum concentration of Pb was found in lentil split (799 ng g^{-1}) and lowest in mong (215 ng g^{-1}), whereas the highest concentration of Cd was found in lentil split (39.0 ng g^{-1} and lowest in gram whole (2.0 ng g^{-1}). The concentration of Pb and Cd in red beans was nearly double than that in the white beans.

Perusal of Table 3 indicates that in the dark coloured pulses (p_1, P_7 and P_{11}), the concentration of Pb and Cd is relatively higher than in the light coloured or white pulses (P_3, P_5 and P_{10}). The data also show that the concentrations of lead and cadmium in samples of split pulses (P_2, P_4, P_6 and P_8) are higher than in the unsplit or whole samples (P_1, P_3, P_5 and P_7). The higher concentrations of Pb and Cd in split samples could be attributed to the contamination of the samples during the mechanical splitting.

Concentrations of Pb and Cd in different types of cereals (C_1-C_7) are tabulated in Table 4 which range from 53-943 (Average 236, median 84) and 47.0-159.2 (Average 75.0, median 74.0) ng g^{-1} respectively. The highest concentration of lead was found in gram flour (943 ng g^{-1}), whereas the highest concentration of Cd was found in corn flour (159.0 ng g^{-1}). The Pb and Cd concentration in flour samples of rice wheat and corn were higher than in their respective grains. The higher concentrations of lead and cadmium in such samples are due to the contamination during milling process, as the contamination of these elements in the samples is proportional to the extent of milling process. This can be observed from the concentration of these elements in samples of gram whole, gram split and gram flour. The average concentration of Pb in pulses is relatively higher than in the samples of rice, wheat and corn. It is also observed that the concentration of lead and cadmium in rice samples is higher than that of the wheat samples. This may possibly be due to the fact that rice crop needs much more water therefore, greater contact time of water with soil resulting the enhance l eaching of these elements and their uptake in the final crop.

Table 5 shows a comparison of Pb and Cd concentrations in wheat, rice and corn with the reported values of other countries [13-18]. The data reveals that the concentration of lead in Pakistani rice samples is higher than

TABLE 2. CONCENTRATION OF LEAD AND CADMIUM IN STANDARD REFERENCE MATERIALS

SRM	Lead		Cadmium	
	Measured value µg g^{-1}	Certified value µg g^{-1}	Measured value µg g^{-1}	Certified value µg g^{-1}
wheat flour NBS-SRM-1567	0.03 ± 0.005	0.02 ± 0.01	0.031 ± 0.008	0.030 ± 0.001
Rice flour NBS-SRM-1568	0.052 ± 0.01	0.045 ± 0.005	0.034 ± 0.001	0.029 ± 0.004
Orchard Leaves	48.3 ± 4.1	45.0 ± 3.0	0.147 ± 0.021	0.110 ± 0.010

TABLE 3. CONCENTRATION OF LEAD AND CADMIUM IN PULSES

Sample Code	Common name	Botanical name	Nature of the sample	Lead ng g^{-1}	Cadmium ng g^{-1}
P_1	Gram	Cicer arietinum	Whole	421 ± 43	2.0 ± 0.3
P_2			Split	444 ± 28	13.7 ± 2.1
P_3	Mong	Phaseolus mungo	whole	215 ± 11	6.5 ± 1.0
P_4			Split	578 ± 24	24.6 ± 2.6
P_5	Mash	Phaseolus radiatus	Whole	341 ± 26	4.0 ± 0.7
P_6			Split	389 ± 4	5.3 ± 0.4
P_7	Lentil	Lenus esculenta	Whole	524 ± 48	9.0 ± 0.9
P_8			Split	799 ± 24	39.0 ± 0.5
P_9	Lentil Malika		Whole	388 ± 17	26.5 ± 2.8
P_{10}	Beans white	Phaseolus leguminous	Whole	307 ± 5	22.2 ± 3.0
P_{11}	Beans Red		Whole	566 ± 28	36.2 ± 2.8

TABLE 4. CONCENTRATION OF LEAD AND CADMIUM IN CEREALS

Sample Code	Common name	Botanical name	Nature of the sample	Lead ng g^{-1}	Cadmium ng g^{-1}
C_1	Rice	Oryza sativa	Grains	121 ± 9	73.0 ± 1.2
C_2			Flour	170 ± 31	86.3 ± 7.8
C_3	Wheat	Triticum vulgare	Grains	53 ± 6	50.0 ± 1.1
C_4			Flour	84 ± 13	74.0 ± 4.7
C_5	Corn	Zea mays	Grains	69 ± 7	47.0 ± 1.4
C_6			Flour	214 ± 30	159.0 ± 11.4
C_7	Gram flour	Cicer arietinum	Flour	943 ± 2	36.2 ± 1.1

TABLE 5. CONCENTRATION OF LEAD AND CADMIUM ng g^{-1} IN CEREALS FROM DIFFERENT COUNTRIES (13-18)

Country name	Concentration of lead Wheat	Rice	Corn	Concentration of cadmium Wheat	Rice	Corn
Pakistan	53	121	69	50	13	47
USA	420-100	-	198-340	70-130	30	-
Japan	50	500	-	20	260	-
China	-	40-100	-	-	130-390	-

those from China but much lower than Japan. The concentration of lead in wheat and corn is much lower than USA. The Cd contents in our rice samples is much lower than China and Japan but higher than USA.

The dietary intake of Pb and Cd was calculated for low, middle and high income group people of urban area. The estimated weekly consumption of pulses and cereals by three different groups is given in Table 6, whereas Table 7. shows the estimated intake values of Pb and Cd through this source. The average concentration of Pb and Cd in each variety of pulses and cereals were used for such calculations. Table 7 indicates that the weekly intake of Pb by people of low and middle income group is almost similar and is relatively higher than the high income group. The intake level for Cd by group A is higher as compared to group B which in turn is higher as compared to group C people. However, all these values are much lower than the tolerance levels of 3500 µg of Pb and 525 µg of Cd [19].

Conclusion

Pb and Cd contents were determined in different varieties of pulses and cereals in order to establish the base line of these elements. This data will be helpful to monitor the

TABLE 6. AVERAGE CONSUMPTION OF PULSES/CEREALS (G/PERSON/WEEK)

S. No.	Common name	A	B	C
1. Pulses				
	(a) Gram	100	80	40
	(b) Mong	100	80	40
	(c) Mash	100	80	40
	(d)Lentil	80	50	40
	(e)Beans	50	50	75
2. Cereals				
	(a) Rice/rice flour	150	350	400
	(b) Wheat/wheat flour	2400	1600	1000
	(c) Corn/corn flour	50	25	20
	(d) Gram flour	25	50	50

A = Low income group., B = Middle income group., C = High income group.

TABLE 7. ESTIMATED WEEKLY INTAKE OF LEAD AND CADMIUM (UG) THROUGH PULSES AND CEREALS

Food commodities	Intake of lead			Intake of cadmium		
	A	B	C	A	B	C
1. Pulses						
(a)Gram	43.2	34.5	17.2	0.8	0.6	0.3
(b) Mong	39.0	31.0	15.6	1.5	1.2	0.6
(c)Mash	36.5	29.2	14.6	0.5	0.4	0.6
(c) Lentil	45.6	28.5	22.8	2.0	1.2	0.6
(e) Beans	21.8	21.8	32.1	1.4	1.4	2.2
2. Cereals						
(a) Rice/Rice flour	21.8	50.9	58.2	12.0	27.8	31.8
(b) Wheat/Wheat flour	164.4	109.6	68.5	148.6	99.0	61.9
(c) Corn/Corn flour	7.1	3.5	2.8	5.1	2.6	2.1
(d) Gram flour	23.5	47.1	47.1	0.9	1.8	1.8
Total Intake.	402.9	356.1	279.5	172.8	136.0	102.3

A = Low income group; B = Middle income group; C = High income group.

degree of contamination. Milling and grinding process induces contamination of lead and cadmium. The data from the present study reflect that Pb and Cd contents in cereals are lower or comparable with those reported from other countries. In view of the rapid industrialization and lack of antipollution regulations in Pakistan, it is desirable to study the levels of these elements in food items from industrialised areas.

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