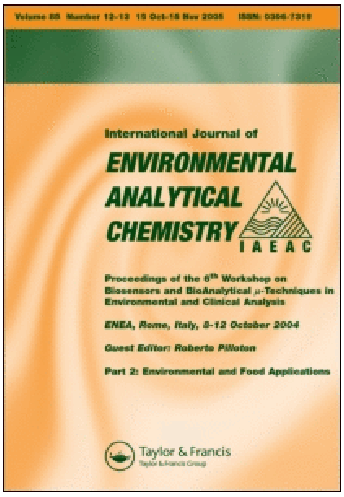

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Determination of Lead and Cadmium in Milk by Electrothermal Atomic Absorption Spectrophotometry

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The concentrations of lead and cadmium in different kinds of milk samples (powdered, infant formula, market, buffalo, condensed and human) were determined using electrothermal atomic absorption spectrophotometric technique. Among all the varieties of milk analysed, condensed milk was found to contain much higher amount of lead. Human milk as expected was found to have lowest concentration of these elements. The results were compared with the reported values of other countries. Daily intake of these toxic elements by adults and babies up to the age of six months through the consumption of various types of milk was estimated and compared with the tolerance levels.

KEY WORDS: Lead, cadmium, electrothermal atomic absorption spectrophotometry, powdered milk, infant formula milk, market milk, buffalo milk, condensed milk, daily intake.

INTRODUCTION

Increasing industrialization and large scale use of agricultural chemicals are polluting the biosphere with foreign chemicals which ultimately find their way to the human body through the food chain. It is, therefore, important to monitor the essential and toxic elements in food items and to establish their baseline levels. The accumulation of toxic elements such as lead and cadmium in the body would adversely affect the physiological functions. For example, higher amounts of lead in the body may cause anemia, apathy, drowsiness, neurological disorder and irreversible renal damage[1] whereas higher amounts of cadmium may induce bone mineralization, anemia and hypertension[2].

Milk is the principal food of infants which normally fulfils all nutritional requirements during early age and is also used frequently by adults. The present large scale production and consumption of dry milk powder, makes it desirable to measure the amount of Pb and Cd in milk, in order to estimate the daily intake of these toxic elements through this source. Determination of trace elements in milk has been reported by various authors using different analytical techniques.[3–6] Atomic absorption spectrophotometry is one of the preferred methods due to its rapidness, high sensitivity and specificity.[7] In the present study the electrothermal atomic absorption spectrophotometric (EAAS) technique was employed for the determination of Cd and Pb in different varieties of milk available in local markets. This study is a continuation of our work on the measurement of essential and toxic trace elements in food items.[8–10]

EXPERIMENTAL

Instrumentation

The measurements were carried out with a Zeiss FMD 3 atomic absorption spectrophotometer equipped with deuterium background corrector and a Perkin-Elmer HGA 74 graphite furnace. Westinghouse hollow-cathode lamps of lead and cadmium were used as radiation sources. Argon was used as an inert purging gas and its flow was interrupted automatically during atomization. The absorption signals during atomization step were recorded as peak heights (in chart units) with a Servager S recorder.

Reagents

Stock solutions (1000 mg/l) of cadmium and lead were prepared by dissolving cadmium chloride monohydrate (BDH) and lead nitrate

(E. Merck) in deionized water. Standard solutions for the construction of calibration curves were prepared by appropriate dilutions of these stock solutions. Fresh working standards were prepared immediately before use. Glassware was cleaned by soaking in nitric acid (1 + 1) for four hours and subsequently rinsed several times with deionized water. Analytical reagent grade perchloric acid and distilled nitric acid[11] were used for digestion of the samples.

Sample collection

Canned whole cream powdered and infant formula milk samples were purchased at random from different shops in Rawalpindi and Islamabad during 1984. Before analysis, samples of the same brands were thoroughly mixed to get homogeneous and representative samples. Market and condensed milk samples obtained from local shops were used as such without any pretreatment. Buffalo milk samples were collected from animals residing near roadside areas and the suburbs of the city. Transitional human milk samples were obtained from five well-to-do urban mothers at the Polyclinic Hospital, Islamabad during May and June 1984. The buffalo and human milk samples were collected directly in cleaned and dried polyethylene stoppered vials and were refrigerated until required for analysis.

Procedure

About 0.5 g of dry and 5.0 g of liquid milk samples were taken in triplicate in 100 ml flasks fitted with 30 cm long air condenser and 6.0 ml distilled nitric acid was added to the sample and then heated at 80°C for 30 min. After cooling, 3.5 ml perchloric acid (70%) was added and then heated again at 250°C with occasional shaking till white fumes evolve. The solution obtained was cooled and transferred into a 25 ml measuring flask and the volume was made up with deionized water, for subsequent measurements of cadmium and lead. A blank was prepared under similar conditions. The standard solution (20 μl) was injected into the graphite tube of the electrothermal analyzer and the programmed dry-ash-atomize sequence was initiated. The various experimental parameters used are listed in Table I.

TABLE I

Conditions for electrothermal a.a.s. measurements of lead and cadmium

	Pb	Cd
Wavelength nm	283.3	228.8
Slit mm	0.3	0.4
Drying Temp. °C	100	100
Time s	60	60
Ashing Temp. °C	700	300
Time s	30	30
Atomization Temp. °C	2100	1900
Time s	10	10
Cleaning Temp. °C	2650	2650
Time s	5	5

A minimum of three injections was used for each solution and the mean values of the absorption signals were used to make the calibration curve. Sample solutions and blank solutions were treated exactly in the same way as the standards. The absorption signals were evaluated by subtracting the mean value of the blank from the signals of the samples.

RESULTS AND DISCUSSION

The concentration of lead and cadmium was determined in seventeen brands of milk including whole cream powdered, condensed, buffalo, market, infant formula and human milk. The results are summarized in Tables II and III. All calculations were made on dry weight basis unless otherwise specified. Five samples were analyzed for each brand of all milk varieties.

To check the accuracy of the procedure an IAEA reference material milk powder (A-8) was analyzed for lead and cadmium under similar experimental conditions. The amounts of lead and cadmium were found to be 0.310 ± 0.008 and $0.053 \pm 0.003\ \mu g/g$, which are in agreement with the IAEA reported information values of 0.220 and $0.03\ \mu g/g$ respectively.

TABLE II

Lead and cadmium contents of various milk samples

Sample no.	Sample code	Conc. of Lead (ng/g)	Conc. of Cadmium (ng/g)
1	P_1	125±21	22±1
2	P_2	173±4	115±7
3	P_3	276±42	26±3
4	P_4	167±11	137±6
5	P_5	15±3	15±0.2
6	P_6	320±14	34±4
7	M_1	20[a]±1	8±1
8	M_2	19[a]±2	11±1
9	C	863[a]±52	3±0.1
10	B_1	238[a]±16	8±1
11	B_2	117[a]±7	10±0.3

[a]Wet weight basis.

TABLE III

Lead and cadmium contents of infant formula milk samples

Sample no.	Sample code	Conc. of lead (ng/g)	Conc. of cadmium (ng/g)
1	I_1	235±35	50±6
2	I_2	257±21	39±3
3	I_3	330±14	59±6
4	I_4	233±25	37±1
5	I_5	23±2	26±4
6	I_6	22±2	9±1
7	H	12[a]±1	6[a]±0.3

[a]Wet weight basis.

The concentrations of lead and cadmium in different brands of whole cream powdered milk samples (P_1–P_6), range from 15–320 (average 179) and 15–137 (average 58) ng/g respectively. These average values are about three times higher than the values of these elements found in Poland,[12] however, the concentration of lead is about one half than that of USA.[13] The average concentrations of lead and cadmium in two commonly used brands of market milk samples (M_1–M_2) were found to be 19.5 and 9.5 ng/g respectively. These values are higher than the reported values of lead (13.4 ng/g) and cadmium (2.9 ng/g) in the bulk milk of Poland.[12] The lead contents are much lower than the values of market milk of Italy (146 ng/g).[14] The average concentration of lead and cadmium in condensed milk (C) was 863 ± 52 and 3.0 ± 0.1 ng/g respectively. The average concentrations of lead and cadmium in milk of buffaloes of road side areas (B_1) were found to be 238 ± 16 and 8.0 ± 1.0 ng/g and that of suburbs (B_2) were 117 ± 7 and 10.0 ± 0.3 ng/g respectively.

Perusal of Table II indicates that the concentration of lead in condensed milk is about five times higher than the average value of whole cream powdered milk which in turn is about nine times higher than that of market milk. The cadmium content of condensed milk is lowest among all the milk samples analyzed whereas whole cream powdered milk contains about six times greater cadmium as compared to market milk. The higher amount of lead and cadmium in whole cream powdered milk and lead in condensed milk could probably be ascribed to the sweetening and canning processes. The higher amount of lead in the milk of buffaloes near roadside areas as compared to the milk of buffaloes in suburbs of the city may possibly be due to the contamination of pasture land by lead arsenate fungicide and the fall out of tetraethyl lead from the gasoline used in vehicles.

The results of six brands of infant formula milk samples (I_1–I_6) are tabulated in Table III. The concentrations of lead and cadmium range from 22–230 (average 183) and 9–59 (average 37) ng/g respectively. The average lead contents of infant formula milk were about four times lower than the reported value of Italy.[15] It was observed that the average concentrations of lead and cadmium in the infant formula milk were nearly equal to that of whole cream powdered milk. The average concentrations of lead and cadmium in transitional human milk samples (H) were found to be 12.0 ± 1.0 and 6.0 ± 0.3 ng/g respectively (Table III). The amount of lead in human milk was less than the reported values of USA (20 ng/g),[13] Poland (26 ng/g)[16] and Malaysia (25.3 ng/g).[17] The cadmium contents were similar to those of Hungary (5.0 ng/g)[18] and Poland (4.0 ng/g)[16] but lower than India (15.0 ng/g).[19] Higher concentration of lead in the human milk as compared to cadmium, may possibly be ascribed to the tendency of lead to pass through the mammary barrier.[20]

The daily intake of lead and cadmium by adults through milk was estimated on the basis of 250 ml consumption of milk per person per day and tabulated in Table IV. The average concentrations of lead and cadmium in each milk variety were used for such calculations. Table IV shows that the intake of cadmium through condensed milk is the lowest, whereas the intake of lead through buffalo and condensed milk are quite higher. All these values are much lower than the tolerance levels of 429 μg of lead and 55–70 μg of cadmium.[21]

TABLE IV

Daily intake of lead and cadmium by adults through milk

Sample no.	Type of milk sample	Intake of lead (μg)	Intake of cadmium (μg)
1	Whole cream powdered[a]	6.71	2.17
2	Market	4.87	2.37
3	Condensed[b]	64.72	0.22
4	Buffalo	44.25	2.25

[a]15 g/100 ml basis.
[b]30 g/100 ml basis.

In order to check whether non-breast fed infants receive the same or different amounts of lead and cadmium as breast fed ones, daily intake of these elements through infant formula, buffalo and human milk is calculated for babies upto six months of age. The results are summarized in Table V along with the recommended frequency and quantity of feed, and body weights. Average concentrations of infant formula milk and buffalo milk were used for the estimation of daily intake of lead and cadmium, whereas for human milk the calculations were based on the assumption that half the amount is equivalent to the recommended amount of powdered or buffalo milk. The data show that the daily intake of lead and cadmium by infants through infant formula or human milk is lower than the recommended tolerable limits of 6.13 μg lead and 0.78–1.00 μg of cadmium per kilogram body weight.[21] The intake of lead through buffalo milk is about three times higher than the tolerance limit, therefore, its

TABLE V

Daily intake of lead and cadmium by infants through milk (μg/kg body weight)

Age in months	No. and amount of feed ml/day	Body weight kg	Lead			Cadmium		
			PM	BM	HM	PM	BM	HM
1	6×90	4.5	3.29	21.24	0.72	0.67	1.08	0.36
2	6×130	6.0	3.57	23.01	0.78	0.72	1.17	0.39
3	5×180	7.5	3.29	21.24	0.72	0.67	1.08	0.36
4	5×205	9.0	3.13	20.16	0.68	0.63	1.02	0.34
5	5×230	10.5	3.01	19.38	0.66	0.61	0.98	0.33
6	5×250	12.0	2.86	18.44	0.62	0.58	0.94	0.31

PM = Powdered Milk (15 g/100 ml); BM = Buffalo Milk; HM = Human Milk.

prolonged use may possibly induce some metabolic abnormalities in infants.

CONCLUSION

Electrothermal atomic absorption spectrophotometric technique was employed to determine the concentrations of lead and cadmium in various types of milk samples. This data will help to establish baseline levels and to monitor the degree of contamination. The daily intake of these elements by adults and infants through milk was also estimated and was found to be within the tolerance limits. The comparison of milk samples from city and suburban areas indicates higher amount of Pb in the milk of buffaloes of city areas. The human milk samples contain relatively higher amounts of Pb as compared to its Cd contents but much lower than that of other types of milk. These studies indicate that the breast fed infants receive less amounts of lead and cadmium than those fed on other types of milk.

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