Pertanika 8(2), 243 – 248 (1985)

# Determination of Cadmium, Lead, Copper and Arsenic in Raw Cocoa, Semifinished and Finished Chocolate Products

C.K. LEE and K.S. LOW
*Chemistry Department,*
*Faculty of Science and Environmental Studies,*
*Universiti Pertanian Malaysia,*
*Serdang, Selangor, Malaysia.*

**Key words: Cocoa bean; chocolate; heavy metal; contamination; allowable limit.**

## ABSTRAK

*Aras kadmium, plumbum, kuprum dan arsenik telah ditentukan dalam dua kelompok koko mentah dan sampel bahan hasil coklat separuh siap di berbagai peringkat perantaraan proses pembuatannya. Kandungan logam untuk lapan belas batang coklat yang dihasilkan oleh empat gudang pembuat coklat telah juga ditentukan. Analisis kandungan logam dalam sampel koko dilakukan secara pengabuan kering sampel itu pada suhu 450°C, kemudian diikuti dengan spektrometri pancaran atom ICP. Purata penemuan semula 90 hingga 97% telah didapati untuk logam yang telah diperlukan pada sampel dengan kepekatan yang diketahui. Kandungan logam yang tidak sekata dalam koko mentah, bahan hasil separuh siap dan bahan hasil siap menunjukkan tiadanya pengotoran berkesan logam semasa proses pembuatannya; amaun logam dalam bahan hasil siap adalah sepadan dengan pecahan yang wujud pada koko. Kandungan logam dalam coklat tempatan yang dihasilkan masih dapat diterima kecuali untuk arsenik di mana amaunnya mendekati nilai yang dihadkan.*

## ABSTRACT

*The levels of cadmium, lead, copper and arsenic were determined in two batches of raw cocoa and semifinished chocolate products sampled at various intermediate stages of the manufacturing process. The metal contents of eighteen chocolate bars produced by four chocolate making factories were also determined. Analyses of the metal contents in cocoa containing samples were effected by dry ashing of the samples at 450°C, followed by inductively coupled plasma atomic emission spectrometry. Average recoveries of 90 to 97% were obtained for the metals when the samples were spiked with known concentrations of metals. The variations in the metal contents of raw cocoa, semifinished and finished products show that there were no effective contaminations of metals during the manufacturing process; the amount of metals in the finished products corresponded to the fraction of cocoa mass present. The metal contents of locally produced chocolates were within acceptable levels except for arsenic which bordered on the limit.*

## INTRODUCTION

The levels of cadmium, lead, copper and arsenic in foodstuff are of interest as these metals are generally considered as toxic to human beings. Information on the analysis of these metals in raw cocoa and finished chocolate products is, however, rather scarce. Knezevic (1979, 1980, 1982) investigated the contents of cadmium, copper, lead and arsenic in cocoa beans from various countries as well as in some chocolate products. He reported a cadmium content of $0.48 - 1.83$ mg kg$^{-1}$ and arsenic content of $0.77$ mg kg$^{-1}$ in Malaysian cocoa beans. These values are higher than those found in beans from South America, Africa and West Indies. The levels of lead (0.21 to 0.42 mg kg $^{-1}$) and copper (21.5 – 32.8 mg kg $^{-1}$) in Malaysian beans were comparable to those from other countries. The metal contents of various chocolate products decreased with the fraction of cocoa mass in the products. Musche and Lucas (1973) studied lead content in some cocoa beans and chocolate products and concluded that there was no lead contamination in the manufacturing process of chocolate products. There is no documented study of cadmium, lead, copper and arsenic levels in locally manufactured chocolate products. The present study reports the determination of the levels of these metals in raw cocoa and intermediate chocolate products in a manufacturing process as well as in some locally manufactured chocolate bars. The suitability of the method of dry ashing followed by analysis by inductively coupled plasma emission spectrometry of these metals in the cocoa samples is also evaluated.

## MATERIALS AND METHODS

Two batches of raw cocoa beans and semifinished products at various intermediate stages were obtained from a chocolate manufacturing factory. The semifinished products included roasted bean, liquor, paste, cake, flake and conch. Half of the raw and roasted beans were deshelled so as to analyse the metal contents in the nibs which were used in chocolate making. The beans and nibs were ground in a stainless steel blender before sampling. The other semifinished products were gently melted over a steam bath to ensure homogeneous sampling.

Eighteen varieties of chocolate bars manufactured by four local chocolate factories were randomly purchased from shops and supermarkets. Only milk and dark chocolate bars were obtained. 2.5 g of cocoa shell and 5.0 g of all the other materials were weighed in acid-washed porcelain crucibles, heated gradually to and maintained at 250°C for 2 hours, and fired at 450°C for 16 hours in a muffle furnace. The ashed products were then wetted with deionized distilled water, treated with 5 cm $^3$ concentrated $HNO_3$, evaporated to dryness on a steam bath, and returned to the furnace at 450°C for 1 hour. The resulting ash was then digested with 5 cm $^3$ of redistilled 6M HCl and made up to 25 cm $^3$ with deionized distilled water. The resulting solutions were analysed for Cd, Pb, Cu and As at wave lengths of 2144.37, 2203.62, 3247.68 and 1937.08 A respectively using a sequential inductively coupled plasma emission spectrometer (Labtest Plasmascan 710). The conditions of operation are as reported by Lee and co-workers (1982). All the samples were prepared in replicates of either two or four.

To determine the suitability of the sample preparation and analysis method, samples of beans, nibs, and liquor were spiked with 1 $\mu$g g $^{-1}$ sample of Cd, 3 $\mu$g g $^{-1}$ sample of Pb and As and 1 $\mu$g g $^{-1}$ sample of copper. Samples of paste, cake, flake and conch were spiked with 0.5 $\mu$g g $^{-1}$ sample of Cd, 1 $\mu$g g $^{-1}$ of Pb and As and 3 $\mu$g g $^{-1}$ sample of Cu. All the spiked samples were duplicated and subjected to the same preparation and analysis procedures as the unspiked samples.

## RESULTS AND DISCUSSION

### *Testing of Method*

The average recoveries (%) of Cd, Pb, Cu and As in spiked samples of cocoa bean, shell, nib and semifinished chocolate products are given in Table 1. When all the cocoa containing samples were considered, mean recoveries of Cd, Pb, Cu and As were 91.9, 97.2, 92.7 and 90.2% respectively. It thus appears that the method of dry ashing at 450°C followed by elemental determination using inductively coupled plasma atomic emission spectrometry (ICPAES) is suitable for the analyses of these metals in raw cocoa and semifinished chocolate products.

As the chocolate bars available in the market are directly moulded from conch, it is reasonable to assume that the sample preparation and analysis method is equally applicable to commercial chocolate bars.

TABLE 1
Average recoveries (%) of metals in spiked samples

| Sample type | Cd | Pb | Cu | As | Average |
|---|---|---|---|---|---|
| Raw bean | 97.6 | 101.0 | 95.9 | 92.7 | 96.8 |
| Roasted bean | 96.2 | 98.0 | 93.5 | 92.8 | 95.1 |
| Raw shell | 89.9 | 95.6 | 93.5 | 90.2 | 92.8 |
| Roasted shell | 92.2 | 98.0 | 89.0 | 90.2 | 92.3 |
| Raw nib | 94.5 | 99.2 | 91.3 | 85.7 | 92.7 |
| Roasted nib | 95.0 | 97.2 | 82.3 | 85.3 | 90.0 |
| Liquor | 90.9 | 91.9 | 100.9 | 84.8 | 92.1 |
| Paste | 92.9 | 98.2 | 100.0 | 92.9 | 96.0 |
| Cake | 89.2 | 97.6 | 93.9 | 94.9 | 95.0 |
| Flake | 87.2 | 95.9 | 90.7 | 90.0 | 90.8 |
| Conch | 84.9 | 96.4 | 88.2 | 93.1 | 90.6 |
| Average | 91.9 | 97.2 | 92.7 | 90.2 | |

Spiked samples were duplicated. RSD's of all duplicates were less than 5%.

*Metal Contents in Raw Cocoa and Semifinished Chocolate Products*

Table 2 lists the levels of Cd, Pb, Cu and As determined in samples obtained from two different batches of chocolate making processes. The raw cocoa beans used in these two batches were from two different sources, and hence the difference in the metal contents. No attempt was made to correct for the difference in moisture contents of the two batches of beans as it was less than 1%.

The levels of Pb (3.54 and 4.25 $\mu g\ g^{-1}$) and As (2.52 and 3.19 $\mu g\ g^{-1}$) in the raw bean were higher than those reported by Knezevic (1980, 1983) whereas the level of Cd was within the range reported (Knezevic, 1979). The levels of Cu (15.22 and 24.50 $\mu g\ g^{-1}$) were comparable to values reported earlier (Knezevic, 1980; Malkus, 1976). The cocoa shells contained more than twice the amount of metals as the nibs. However as the shells were discarded in the chocolate manufacturing process, they did not contribute to the metal contents in the semi-finished and finished products.

The metal contents in liquor and cocoa nib were similar as expected and decreased tremendously from liquor to paste. This was the result of dilution by the addition of other ingredients at this intermediate stage. The increase in metal contents from paste to cake was due to loss of moisture in the heating process, and the decrease from cake to flake was due to further addition of other ingredients. Conch and flake contained practically similar amounts of metals.

From the variations in the metal contents from one intermediate stage to another, there did not seem to be contamination of metals, either from the processes involved or from the ingredients added.

*Metal Contents in Chocolate Bars*

There are four major chocolate producing factories in Malaysia. These factories produce milk chocolate bars (with and without nuts) of various sizes, dark chocolate bars as well as cooking chocolate. In the present study, only plain milk and dark chocolate bars were considered.

TABLE 2

Metal contents ($\mu g\ g^{-1}$) in raw beans and semifinished chocolate products

| Sample | Cd | | Pb | | Cu | | As | |
|---|---|---|---|---|---|---|---|---|
| | Batch 1 (SD) | Batch 2 (SD) | Batch 1 (SD) | Batch 2 (SD) | Batch 1 (SD) | Batch 2 (SD) | Batch 1 (SD) | Batch 2 (SD) |
| Raw bean | 0.89 (0.01) | 1.10 (0.01) | 3.54 (0.01) | 4.25 (0.09) | 15.22 (0.90) | 24.50 (0.05) | 2.52 (0.02) | 3.19 (0.01) |
| Roasted bean | 0.98 (0.01) | 1.09 (0.01) | 4.02 (0.05) | 4.09 (0.04) | 15.89 (0.90) | 24.33 (0.48) | 2.43 (0.03) | 3.04 (0.01) |
| Raw shell | 1.32 (0.06) | 2.05 (0.01) | 6.15 (0.10) | 8.28 (0.10) | 16.79 (0.25) | 25.02 (0.35) | 5.81 (0.02) | 7.45 (0.01) |
| Roasted shell | 1.53 (0.01) | 2.11 (0.11) | 7.21 (0.01) | 9.14 (0.14) | 17.23 (0.04) | 27.10 (0.64) | 6.32 (0.08) | 7.85 (0.20) |
| Raw nib | 0.76 (0.02) | 1.01 (0.01) | 3.00 (0.05) | 3.62 (0.01) | 10.89 (0.01) | 24.54 (1.3) | 1.96 (0.04) | 2.65 (0.01) |
| Roasted nib | 0.79 (0.01) | 0.99 (0.01) | 3.28 (0.06) | 3.57 (0.04) | 16.82 (0.46) | 17.43 (0.12) | 1.95 (0.01) | 2.49 (0.03) |
| Liquor | 0.75 (0.05) | 0.98 (0.01) | 3.13 (0.11) | 4.30 (0.01) | 13.78 (0.28) | 18.28 (0.42) | 1.92 (0.11) | 2.60 (0.02) |
| Paste | 0.28 (0.01) | 0.27 (0.01) | 1.34 (0.01) | 1.26 (0.01) | 2.54 (0.12) | 2.87 (0.05) | 0.59 (0.01) | 0.84 (0.00) |
| Cake | 0.30 (0.01) | 0.34 (0.01) | 1.49 (0.09) | 1.52 (0.03) | 2.76 (0.04) | 4.05 (0.08) | 0.84 (0.02) | 1.08 (0.01) |
| Flake | 0.26 (0.01) | 0.28 (0.01) | 1.28 (0.03) | 1.34 (0.07) | 2.70 (0.03) | 4.22 (0.16) | 0.75 (0.01) | 1.08 (0.01) |
| Conch | 0.27 (0.01) | 0.30 (0.01) | 1.28 (0.08) | 1.33 (0.04) | 2.45 (0.06) | 4.73 (0.60) | 0.55 (0.01) | 1.08 (0.04) |

Beans used in batch 1 and 2 were from different sources.

Metals contents for batch 1 and 2 are means of 2 and 4 replicates respectively.

TABLE 3
Metal content ($\mu g\ g^{-1}$) in chocolates

| Chocolate | Type | Cd(SD) | Pb(SD) | Cu(SD) | As(SD) |
|---|---|---|---|---|---|
| A1 | Milk chocolate | 0.32 (0.01) | 1.55 (0.05) | 3.30 (0.29) | 0.96 (0.04) |
| A2 | Milk chocolate | 0.31 (0.02) | 1.36 (0.07) | 3.92 (0.24) | 0.91 (0.05) |
| A3 | Dark chocolate | 0.39 (0.06) | 1.82 (0.26) | 5.17 (0.74) | 1.14 (0.24) |
| A4 | Dark chocolate | 0.30 (0.01) | 1.74 (0.25) | 4.12 (0.26) | 0.98 (0.04) |
| A5 | Orange flavoured milk chocolate | 0.30 (0.02) | 1.34 (0.12) | 2.92 (0.60) | 0.90 (0.02) |
| A6 | Orange flavoured milk chocolate | 0.29 (0.01) | 1.45 (0.08) | 3.35 (0.14) | 0.94 (0.03) |
| A7 | Chunky milk chocolate | 0.28 (0.00) | 1.42 (0.14) | 3.49 (0.16) | 0.93 (0.01) |
| A8 | Chunky milk chocolate | 0.28 (0.01) | 1.45 (0.12) | 3.74 (0.15) | 0.89 (0.04) |
| A9 | Cooking chocolate | 0.42 (0.01) | 1.93 (0.16) | 6.34 (0.49) | 1.15 (0.01) |
| B1 | Milk chocolate | 0.32 (0.01) | 1.29 (0.04) | 3.79 (0.49) | 0.90 (0.05) |
| B2 | Milk chocolate | 0.28 (0.01) | 1.35 (0.01) | 3.59 (0.17) | 0.86 (0.02) |
| B3 | Milk chocolate | 0.26 (0.01) | 1.10 (0.04) | 3.37 (0.16) | 0.84 (0.01) |
| B4 | Milk chocolate | 0.29 (0.01) | 1.30 (0.03) | 3.77 (0.03) | 0.87 (0.04) |
| C1 | Milk chocolate | 0.42 (0.01) | 1.90 (0.05) | 3.78 (0.21) | 1.28 (0.03) |
| C2 | Milk chocolate | 0.36 (0.01) | 1.55 (0.10) | 4.62 (0.27) | 1.13 (0.02) |
| C3 | Milk chocolate | 0.41 (0.01) | 1.94 (0.03) | 3.95 (0.02) | 1.28 (0.01) |
| D1 | Milk chocolate | 0.28 (0.01) | 1.26 (0.06) | 3.49 (0.16) | 0.86 (0.05) |
| D2 | Milk chocolate | 0.28 (0.02) | 1.19 (0.03) | 3.18 (0.16) | 0.83 (0.02) |

All values are means of four replicates.
A, B, C and D denote four different chocolate manufactures.

Table 3 gives the analysis results of these chocolate bars. The mean values of Cd, Pb, Cu and As in all the samples studied were 0.32, 1.50, 3.88 and 0.98 $\mu g\ g^{-1}$ respectively. There was no great variation in the metal contents of the milk chocolate bars studied. However, the dark and especially the cooking chocolates contained higher metal contents. This indicates that the higher the fraction of cocoa mass in the finished product, the higher its metal contents. It also suggests that addition of ingredients like milk powder and sugar does not contribute effectively to the metal contents of the finished products. Similar observations have been made by Knezevic (1979) and Lucas and Musche (1973).

The levels of Cd and Cu in the chocolate products studied fell within the ranges of those reported by Knezevic for German products (1979, 1982), namely 0.02 to 0.69 and 4.80 to 24.30 $\mu g\ g^{-1}$ respectively. Malkus (1976) reported Cu content of 3.2 – 13.6 ppm in Czechoslovakian chocolate products. Knezevic (1980) reported lead levels of 0.02 to 0.69 $\mu g\ g^{-1}$ in milk, semi bitter and bitter chocolates investigated. Ruggerti *et al.*, (1983) reported that two commercial cocoa and six chocolate products contained 1.65 to 1.85 ppm of Pb and 0.04 to 0.06 ppm of Cd. Pb content in the chocolate products in our study was thus higher than that reported by Knezevic but comparable to that reported by Ruggerti *et al.* The As content obtained in the present study was higher that that reported by Knezevic (1982). According to the Malaysian Standards (1984), the limits for Cu, Pb and As in cocoa powder are 50, 2 and 1 ppm respectively. Applying these limits on the locally manufactured chocolate products, the levels of Cu, Pb and As, on the whole, are acceptable.

*Correlation of Metals*

The relationship between each pair of the metals studied was examined using Pearson Correlation programme of the SPSS package (Nie *et al.*, 1975). Table 4 gives the correlation coefficients and the significance levels on the application of t-test. It appears that all the metals were strongly correlated with each other. This indicates that the metals were from the same source. This further strengthens the suggestion that the source of metal contents was not contamination from the manufacturing process, but the raw bean itself.

TABLE 4
Matrix of correlation coefficients for metal contents in the chocolates

| | Pb | Cu | As |
|---|---|---|---|
| Cd | 0.89*** | 0.67** | 0.95*** |
| Pb | | 0.62* | 0.93*** |
| Cu | | | 0.57* |

n = 18
Level of significance: * $P \leqslant 0.05$
** $P \leqslant 0.005$
*** $P \leqslant 0.0005$

## CONCLUSION

The analysis method used in the present study was found to be suitable for cocoa containing materials.

The levels of Cd, Pb, Cu and As in raw cocoa beans appeared high. A systematic and thorough survey of these metal contents in Malaysian cocoa beans is required to determine their variations and distribution patterns. Work in this area is currently in progress.

Metal contents of locally produced chocolates are within accpetable levels. No contamination of metals during the manufacturing process was observed.

## ACKNOWLEDGEMENT

The authors wish to thank Majlis Penyelidikan dan Kemajuan Sains Negara (MPKSN) for financing this research project. Thanks are also due to Ms Choo Chai Syam for preparing the cocoa containing samples for analysis.

## REFERENCES

KNEZEVIC, G. (1979): Heavy metals in food. Part 1. Content of cadmium in raw cocoa beans and in semifinished and finished chocolate products. *Dtsch. Lebensm — Rundsch,* **75(10)**: 305 – 9.

KNEZEVIC, G. (1980): Heavy metals in food stuff. The copper content of raw cocoa, intermediate and finished cocoa products. *CCB,* **5(2)**: 24 – 6.

KNEZEVIC, G. (1982): Heavy metals in food. Part 2. Lead content in unrefined cocoa and in semifinished and finished cocoa products. *Dtsch,* Lebensm-Rundsch, **78(5)**, 178 – 180.

KNEZEVIC, G. (1982): Determination of arsenic in cocoa containing foods by hydride generation AAS. *Zuker-Suesswaren Wirtsch,* **35(6)**: 199 – 200.

LEE, C.K., LOW, K.S. and HOH, R. (1982): An evaluation of an inductively coupled plasma (ICP) emission spectrometer. *Pertanika,* **5(1)**: 39 – 44.

LUCAS, W. and MUSCHE, R. (1973): Heavy metal contamination of foods 2. Lead content of cocoa products. *Dtsch, Lebensm-Rundsch,* **69(12)**: 460 – 461.

MALKUS, Z. (1976): Copper in Czechoslovakian and some foreign chocolate products. *Cesk. Hyz.* **21(3)**: 119 – 123.

MUSCHE, R. and LUCAS, W. (1973): Heavy metal contamination of foods I. Cocoa beans. *Dtsch. Lebensm-Rundsch,* **69(8)**: 227 – 278.

NIE, N.H., HULL, C.H., JENKINS, J.G., STEINBRENNER, K. and BENT, D.H. (1975): Statistical package for the social science. Second edition Toronto, Mc Graw-Hill.

RUGGERTI, P., FONSECA, G, RUGGERTI, G. (1983): Theobromine and caffeine content and lead content and cadmium presence in cocoa products. *Ind. Aliment.* **22(10)**: 720 – 722.

SPECIFICATION FOR MALAYSIAN COCOA POWDER, MS 871, (1984): Standards and Industrial Research Institute Malaysia. (In press).

*(Received 19 February, 1985)*