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# Analysis of heavy metals in citrus juice from the Abura-Asebu-Kwamankese District, Ghana

**J. K Tufuor *, J. K. Bentum, D.K. Essumang, J. E. Koranteng -Addo**

*Department of Chemistry University of Cape Coast, Cape Coast, Ghana*

## ABSTRACT

*The levels of some heavy metals in lime, lemon and orange fruit juice from the Abura-Asebu-Kwamankese District of the Central Region of Ghana were determined. Samples were randomly collected from selected farms in the district. The samples were digested with HCl and $HNO_3$ mixture (aqua regia) and $H_2O_2$ and analysed for AS, Pb, Cr, Ni, Fe, Zn and Cu using Inductive Coupled Plasma (ICP) Atomic Emission Spectrophotometer. Fe, Zn, and Pb were found in all the samples with mean concentrations respectively 1.2065, $2.401\times10^{-1}$ and $2.92\times10^{-2}$ ppm. Cu and As were found in the lime only with concentrations $4.313\times10^{-3}$ and $1.092\times10^{-3}$ ppm respectively. Cr and Ni were not detected in any of the samples analysed. The concentrations of the metals found in all the three fruits were far lower than those Dietary reference values for food energy and nutrients levels recommended in the United Kingdom and by the US EPA.*

**Key Words:** Abura-Asebu-Kwamankese District, heavy metals, chromium, nickel, arsenic, zinc, cupper, lead, iron, orange, lemon and lime.

## INTRODUCTION

Heavy metal contamination of fruits, vegetables and other crops are a major concern since their accumulation in food crops in higher concentrations could cause serious risk to human health if the crops are consumed [1, 2]. Such accumulation has been reported by Okoronko [3]. Arsenic, lead, zinc and other metals have been detected in food crops at levels that exceed the recommended dietary allowance. Although many heavy metals do not play any significant role in the body of plants, metals like copper, zinc and iron are essential elements in the body of the

plant due to their physiological functions. The essential elements are very important because they are involved in many enzymes systems in the human body. However, high concentrations are toxic [4].

The sources of these metals in food crops include discharges onto agricultural lands, wastewater from industries and sewage, application of some pesticides, metal aerosol deposition from the atmosphere due to emissions from vehicles and other sources. These trace metals are also translocated from the soil solution through the roots to other parts of the plant [5-7]. Cultivation of Citrus crops is a major source of income for many farmers in the district. Also the leading exporter of lime juice in Ghana and some citrus processing factories obtain their raw materials from the district. Accumulation of these heavy metals in the crops in higher concentrations could cause serious risk to human health if the crops are consumed and also adversely affect export. The objective of the study therefore was to:

- Determine the levels of As, Pb, Cr, Ni, Cu, Zn and Fe in orange, lime and lemon fruits grown in the Abura-Asebu-Kwamankese District in Ghana.

- Compare the concentrations of the various metals determined in this study with recommended dietary reference values for food energy and nutrients levels in other countries.

## EXPERIMENTAL SECTION

*Sample collection*

Oranges, limes and lemons samples were collected randomly from different farms, in the Abura-Asebu –kwamankese District of the Central Region of Ghana, and placed into appropriately labelled sacks and conveyed to the laboratory for analysis. For each citrus variety, four samples were obtained for each variety.

*Sample treatment*

The fruits were washed with tap water and then with distilled water after which the juice were squeezed into separate beakers. About 200 mL of juice was obtained from each sample. The juice were filtered, mixed well and then stored in a refrigerator prior to analysis. 50 mL of sample was placed into a 250 mL beaker. 50 mL of aqua regia prepared from analytical grade concentrated 36% HCl and concentrated 63% $HNO_3$ was added. The mixture was covered with a watch glass, heated and reflux on a hot plate. Additional 10 mL of the aqua regia was added and the heating continued until the colour was very light yellow. The last step was repeated and the solution evaporated until the volume was about 15-20 mL. The solution was cooled and 10 mL of 30% $H_2O_2$ (AR) added and heated without boiling until effervescence was minimal to ensure complete digestion. The heating was continued and the volume reduced to about 10 mL. The beaker was removed from the hot plate cooled and the walls washed down with double distilled. The digest was filtered using Whatman No. 4 filter paper into a 50 mL volumetric flask and then diluted with double distilled water to the 50 mL mark. Four samples each of the juice from orange, lemon and lime, and also the spiked samples and blank were digested using this method. All the digested samples were analysed for As, Pb, Cr, Ni, Fe, Cu and Zn using Inductive Coupled Plasma Atomic Emission Spectrometer (ICP).

**Recovery and Reproducibility Studies**

To validate the method of analysis, the precision of the instrument used and the efficiency of the method used in the chemical analysis were determined. The recovery and reproducibility studies were conducted using standards of known concentrations. In the reproducibility studies, known certified concentrations (1.0 ppm) of As, Pb, Cr, Ni, Fe Cu and Zn in double distilled water were analysed separately using Inductive Coupled Plasma Atomic Emission Spectrometer (ICP). The efficiency of the digestion process was determined by analysing the percentage of metal recovered from spiked samples. A blank and standards were use to zero and calibrate the instrument after which the spiked were analysed.

**Table 1: Reproducibility of recovery of metals from aqueous solution spiked with 1.0 ppm of metal**

| | Concentration of metal recovered ( ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Arsenic | Lead | Chromium | Nickel | Iron | Copper | Zinc |
| 1 | 0.958 | 0.978 | 0.987 | 0.965 | 1.011 | 0.974 | 0.975 |
| 2 | 0.967 | 0.971 | 0.977 | 0.977 | 1.020 | 0.968 | 1.021 |
| 3 | 0.957 | 1.013 | 1.100 | 0.968 | 0.959 | 0.969 | 1.010 |
| 4 | 1.010 | 1.002 | 0.978 | 0.968 | 0.967 | 1.011 | 0.987 |
| Mean | 0.973 | 0.991 | 1.010 | 0.968 | 0.897 | 0.981 | 0.998 |
| SD | ± 0.025 | ± 0.019 | ± 0.059 | ± 0.059 | ±0.000 | ± 0.021 | ± 0.021 |

**Table2: Concentration of metal recovered from four samples of lime juice spiked with 2.0 ppm of metal**

| Spiked Lime juice | Concentration of metal recovered ( ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Arsenic | Lead | Chromium | Nickel | Iron | Copper | Zinc |
| 1 | 1.957 | 1.968 | 1.902 | 1.965 | 1.887 | 1.969 | 1.974 |
| 2 | 1.947 | 1.978 | 2.010 | 1.987 | 1.898 | 1.888 | 1.891 |
| 3 | 2.000 | 1.979 | 1.984 | 2.002 | 1.969 | 1.968 | 1.989 |
| 4 | 1.958 | 1.988 | 1.995 | 1.898 | 1.956 | 2.008 | 1.986 |
| Mean | 1.966 | 1.978 | 1.973 | 1.963 | 1.928 | 1.958 | 1.960 |
| SD | ± 0.023 | ± 0.008 | ± 0.048 | ± 0.046 | ± 0.041 | ± 0.041 | ± 0.046 |
| RSD % | 1.170 | 0.404 | 2.433 | 2.343 | 2.127 | 2.094 | 2.347 |
| Recovery% | 98.28 | 98.91 | 97.73 | 98.15 | 96.40 | 97.91 | 98.00 |

*Limit of Detection (LOD) = 0.001ppm, Accuracy (as % recovery) at 2.0 ppm*

The mean percent recovery of spiked elements for all samples range between 96.40% ± 0.048 and -98.91 ± .008

## RESULTS AND DISCUSSION

The results of the determination of the concentrations of metal in the fruit juice are shown in tables 3-5.

The results of the analysis are shown in tables 3-6. Generally the mean concentrations of the metals in all the three samples were as follows: As, $1.092\times10^{-3}$ ; Cu $4.313\times10^{-3}$ :Pb $2.92\times10^{-2}$; Fe 1.2065; and Zn $6.0\times10^{-2}$ ppm, Cr and Ni were not detected in any of the samples. The ranges of the metals detected in all the three types of citrus were; As $1.12\times10^{-2}$-$1.68\times10^{-2}$; Pb $5.0\times10^{-2}$-$.3.486\times10^{-1}$; Fe $4.27\times10^{-1}$ – 1.665; Cu 1.0 $\times10^{-2}$- $1.07\times10^{-2}$ and Zn 9.14 $\times10^{-2}$– $4.40\times10^{-1}$ ppm. Apart from Pb which was found to be highest in the lemon juice, with mean 0.3015 ppm, and

lowest in the orange, the concentrations of all the other metals As, Fe and Zn and Cu were highest in the lime juice and least in the orange juice.

**Table 3: Concentration of metal in orange juice**

| Orange | Concentration of metal orange juice ( ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Arsenic | Lead | Chromium | Nickel | Iron | Copper | Zinc |
| $G_1$ | Nd | nd | nd | nd | 0.6171 | nd | 0.1354 |
| $G_2$ | Nd | nd | nd | nd | 0.4275 | nd | 0.1128 |
| $G_3$ | Nd | 0.050 | nd | nd | 0.4841 | nd | 0.0914 |
| $G_4$ | Nd | nd | nd | nd | 0.8171 | nd | 0.1184 |
| Mean | Nd | 0.013 | nd | nd | 0.5865 | nd | 0.1145 |
| SD | | ± 0.021 | | | ± 0.173 | | ± 0.018 |

**Table 4: Concentration of metals in lime juice**

| Lime juice | Concentration of metal in lime juice ( ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Arsenic | Lead | Chromium | Nickel | Iron | Copper | Zinc |
| $L_1$ | 0.0131 | 0.1091 | nd | nd | 1.5970 | nd | 0.4400 |
| $L_2$ | 0.0112 | 0.0328 | nd | nd | 1.6650 | 0.100 | 0.2531 |
| $L_3$ | 0.0168 | nd | nd | nd | 1.5360 | 0.107 | 0.2989 |
| $L_4$ | 0.0113 | 0.0297 | nd | nd | 1.4810 | nd | 0.3196 |
| Mean | 0.0131 | 0.0429 | nd | nd | 1.5700 | 0.0518 | 0.3279 |
| SD | ± 0.003 | ± 0.038 | | | ± 0.073 | ±0.0598 | ± 0.0797 |

**Table 5: Concentration of metal in lemon juice**

| Lemon juice | Concentration of metal in lemon juice ( ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Arsenic | Lead | Chromium | Nickel | Iron | Copper | Zinc |
| $M_1$ | Nd | 0 0.3029 | nd | nd | | nd | 0.3176 |
| $M_2$ | Nd | 0.3486 | nd | nd | 1.5069 | nd | 0.2981 |
| $M_3$ | Nd | 0.2530 | nd | nd | 1.5504 | nd | 0.2961 |
| $M_4$ | Nd | 0.3001 | nd | nd | 1.4707 | nd | 0.1999 |
| Mean | Nd | 0.3015 | nd | nd | 1.4630 | nd | 0.2779 |
| SD | | ± 0.039 | | | ± 0.0982 | | ± 0.059 |

Generally the metals detected were found to be highest generally in the lime juice (fig.1) probably due to its high acidity and sequenstration ability. These fruits contain fruit acids such as Citric, tartaric, and malic acids that have the power of chelating heavy metals. The chelating power partly depends on the acidity of the fruit, and since the acidity of the three citrus fruits has been found to be in the order lime> lemon > orange [8-9], it is therefore not surprising that the lime had the highest concentration of trace metals. The mean concentrations of the trace metals were found to be in the order; As< Cu< Pb <Zn < Fe. The order of the non essential elements was (< 0.001ppm) <As < Pb while that of the essential elements was Cu< Fe< Zn, (fig.1). Cr and Ni were not detected in any of the samples analyzed probably because their concentrations were below the detection limit {LOD=0.001 ppm).

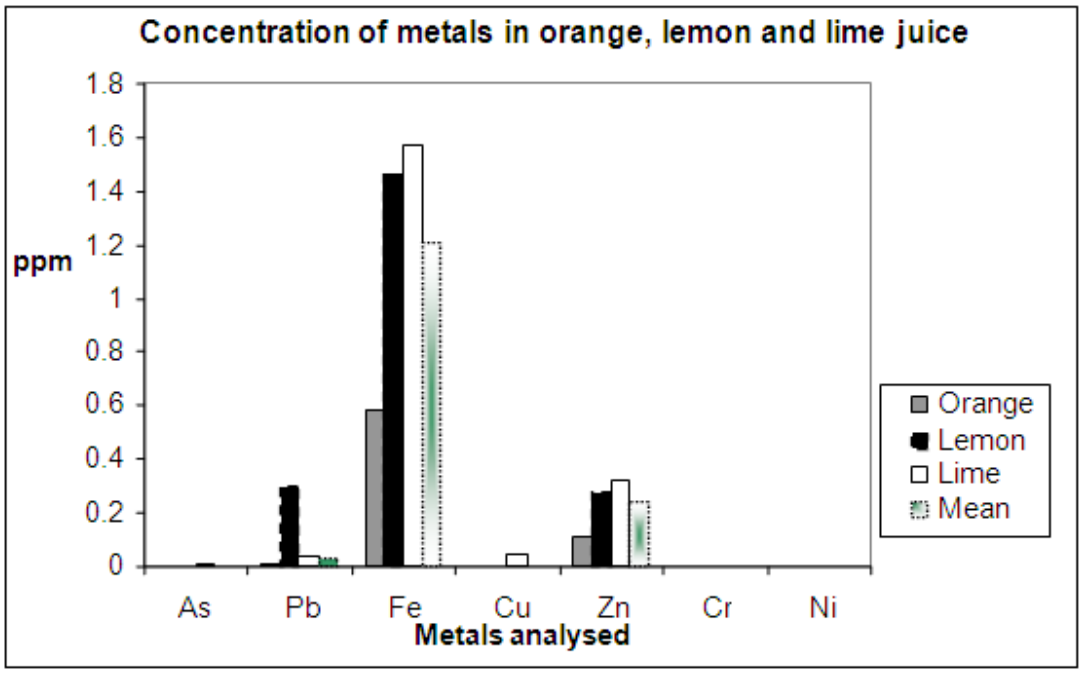


**Figure 1: Concentration of some heavy metals in orange, lemon and lime fruits from Abura- Asebu-Kwamankese District of Ghana**

The concentrations of the metals found in all the three fruit were far lower than those Dietary reference values for food energy and nutrients levels recommended in the United Kingdom by the Department of Health committee on medical aspect of food policy and the US EPA [10-17]

Though there were correlations among the metals in all the fruits, most of these were not significant at the 0.05 level. The significant correlations observed were very high, and these were between Cu and each of the metals Fe, As and Zn in the lime juice. In each case the value of r was 1.0 at the 0.01 confidence level.

## CONCLUSION

The results obtained indicate that traces elements, both essential and non essential heavy metals were present in citrus fruits from the Abura- Asebu- Kwamankese District of Ghana. Fe, Zn, Pb, Cu and As were detected in the citrus fruits analysed, with mean concentrations 1.2065, $2.401\times10^{-1}$, $2.92\times10^{-2}$ ppm, $4.313\times10^{-3}$ and $1.090\times10^{-3}$ ppm respectively. Cr and Ni were not detected in any of the samples. The levels of the essential metals Cu, Zn and Fe were far below the recommended daily intake. It is therefore safe to consume oranges, lemons or limes from the Abura- Asebu- Kwamankese District of Ghana since the levels of all the metals found in them were far lower than dietary reference values recommended by the United Kingdom Department of Health and the US EPA.

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