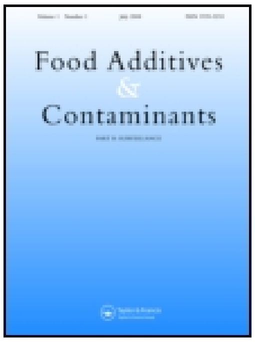


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# Levels of selected heavy metals in canned tomato paste sold in Ghana

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Sixty-one samples of canned tomato paste comprising seven brands originating from three countries and sold in local markets in the Kumasi Metropolis of Ghana were analysed for levels of iron (Fe), zinc (Zn), manganese (Mn), cadmium (Cd) and lead (Pb) by flame atomic absorption spectrophotometry and for levels of mercury (Hg) by direct mercury analyzer. Mean heavy metal concentrations varied by brand, ranging from below the limit of detection (Cd) to a maximum concentration range of $1.68 \pm 1.63$ to $58.6 \pm 14.5\,\mu g\,g^{-1}$ (Fe). Estimated mean ranges of other heavy metals are $2.06 \pm 0.62$ to $8.52 \pm 0.68\,\mu g\,g^{-1}$ (Zn), $2.62 \pm 0.33$ to $5.75 \pm 0.47\,\mu g\,g^{-1}$ (Mn), $0.070 \pm 0.003$ to $0.116 \pm 0.012\,\mu g\,g^{-1}$ (Pb) and $0.011 \pm 0.001$ to $0.102 \pm 0.001\,\mu g\,g^{-1}$ (Hg). Assessed metal levels in five brands were below the WHO/FAO permissible levels. Results of the one-way analysis of variance (ANOVA) conducted on the data suggested no significant variations ($P > 0.05$) in the concentrations of the metals in the same brands of canned tomatoes.

**Keywords:** canned foods; vegetables; heavy metals

## Introduction

Canned tomato pastes are one of the most frequently consumed canned vegetables in the Ghanaian diet, affording taste, colour, vitamin and mineral benefits (Canene-Adams et al. 2005; Akbudak et al. 2009). However, they may also constitute a source of dietary exposure to heavy metal toxicants. Heavy metals may be present in canned tomato paste through uptake by plants from contaminated soil, from polluted water or from applied agrochemicals. Harvested fruits may also become contaminated during canning processes or via leaching from the metal containers into the canned product during storage (Nincević et al. 2009). Heavy metals may also contaminate processed tomato paste through the addition of preservatives, stabilisers and synthetic colouring agents (Oduoza 1992).

Ingested heavy metal toxicants at concentrations above the threshold of risk are associated with the etiology of some diseases. Acute Zn toxicity may cause gastrointestinal distress, diarrhea, abdominal pain, nausea and vomiting (Venugopal and Luckey 1975). Chronic exposure of humans to Cd is associated with development of chronic obstructive pulmonary disease and is a major contributor to cancer risk (Venugopal and Luckey 1975). Pb toxicity can lead to nervous system dysfunction, growth retardation, neuronal defects and anaemia in children (Venugopal and Luckey 1975). Chronic exposure to Hg contributes to increased risk of cardiovascular disease (Venugopal and Luckey 1975). Levels of Fe and Mn above the threshold of risk are associated with nervous system dysfunctions (Venugopal and Luckey 1975).

Food contamination by heavy metals therefore constitutes a significant health hazard because the metals tend to persist and to bio-accumulate, leading to amplification of its concentrations in target tissues and organs and to the onset of associated diseases (Nishihara et al. 1985). Although the concentrations and incidences of heavy metals in canned tomato paste have been assessed in other parts of the world, no complementary study exists in Ghana (Al-Khalifa 1997; Türker and Yüksel 1997; Waheed et al. 2003; David et al. 2008; Melaku 2009; Itodo and Itodo 2010). Estimation of heavy metal levels in canned tomato in Ghana will determine whether this dietary exposure is within the safe regulatory exposure limits. Assessment of the levels of heavy metals in canned tomatoes in Ghana is thus an area of study that warrants investigation. This study estimates the total concentration of six heavy metals (Hg, Pb, Cd, Fe, Mn and Zn) in seven brands of canned tomato paste sold in the Kumasi metropolis of Ghana.

## Materials and methods

### *Sample collection*

Sixty-one retail samples of tomatoes paste comprising seven different brands and representing three countries

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of origin (China, Ghana and Singapore) were randomly purchased from different local outlets in Kumasi, Ghana, in 2006. The retail outlets include street markets, grocery shops and supermarkets sited at Adum, Kejetia, Asafo, Bantama, Ayigya, Atonsu and New Tafo suburbs of Kumasi, Ghana. The samples cover all the available brands in the retail market. All samples were packaged in lead soldered cans. Each canned product weighed 70 g. Samples were transported to the laboratory at the KNUST and frozen at −20°C until analysis. Prior to analysis, samples were coded by brand as PT ($n = 11$), VT ($n = 5$), LT ($n = 9$), FT ($n = 8$), NT ($n = 10$), OT ($n = 5$) and GT ($n = 13$). Since the emphasis of sampling is in obtaining samples that reflect the broad range of tomato paste consumed in the Ghanaian home, production lots and the storage times of samples were not controlled in this study. All samples were within the expiry date displayed on the respective can.

### *Reagents*

All reagents were of analytical reagent grade. HCl, $H_2SO_4$ and $HNO_3$ were purchased from BDH (London, UK). Titrasol (1000 mg $L^{-1}$) stock solutions of heavy metals were purchased from Merck (Stuttgart, Germany). DORM-2 certified reference solutions of elements were obtained from the National Research Council of Canada (NRCC).

### *Instrumentation*

A cold vapour atomic absorption spectrophotometer equipped with an automatic Direct Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan) was used for Hg analyses. Signal outputs were captured on a Yokogawa Model 3021 strip chart recorder. A UNICAM Model 929 flame atomic absorption spectrometer (FAAS) equipped with a deuterium background corrector and air-acetylene burner (Unicam Analytical System, Cambridge, UK) was used for Pb, Cd, Zn, Mn and Fe analyses.

### *Method description*

All glassware was soaked overnight in 10% (v/v) nitric acid followed by washing with 10% (v/v) hydrochloric acid. Acid-washed glassware was rinsed with double-distilled water and oven dried before use. Double-distilled water was used wherever water is specified.

### *Preparation of solutions*

Standard stock solutions of mercury, cadmium, lead, zinc, manganese and iron were prepared from Titrasol (1000 mg $L^{-1}$) by dilution to the desired concentrations for the corresponding metals with water. Working solutions were freshly prepared by diluting an appropriate aliquot of the stock solutions with 10% $HNO_3$ (for the determination of Cd, Pb, Zn, Mn and Fe) and with the acid mixture of 1 M HCl and 5% $H_2SO_4$ (for the determination of Hg). Stannous chloride solution (10% w/v), for Hg determination, was prepared by dissolving 10 g of the salt in 100 mL 1 M HCl. Nitrogen gas at 50 mL $min^{-1}$ was bubbled through the stannous chloride solution for 30 min.

### *Sample preparation*

For the determination of Hg, 2 g of each sample was weighed into a 0.5−L glass digestion tube, and 10 mL of concentrated $HNO_3/HClO_4$ (1:1) and 5 mL of concentrated $H_2SO_4$ were slowly added. The tube was then placed on top of a steam bath unit and samples were allowed to dissolve completely. The digest was removed from the steam bath, cooled and filtered. A 10 mL solution of stannous chloride (10% w/v) was added to the filtered solution before carefully transferring it into a 50-mL volumetric flask. The flask was diluted to the mark with distilled water.

For the determination of Pb, Cd, Zn, Mn and Fe, 2 g of the sample was weighed into a 200-mL beaker and 10 mL of concentrated $HNO_3$ was added. The beaker was covered with a watch glass and the sample was allowed to digest in the acid overnight. The dissolved sample was heated on a hot plate until all vigorous reactions subside and a clear solution obtained. The digest was allowed to cool, transferred into a 50-mL volumetric flask and diluted to the mark with distilled water.

### *Elemental analysis of samples*

Metal levels were determined directly on each final solution. For Hg level determination, 5 mL of each sample was injected into the direct mercury analyzer on the cold vapor atomic absorption spectrophotometer and signals recorded. Calibration standard solutions, reagent blanks and reagent blank spikes for Hg were analysed in the same way as the sample. Pb, Cd, Zn, Mn and Fe levels were determined by direct aspiration of the sample solution into the air-acetylene flame of the UNICAM 969 FAAS. Calibration standard solutions, reagent blanks and reagent blank spikes for each metal were analysed in the same way as the sample.

Samples were run in seven analytical batches, with each analytical batch consisting of four standards, three reagent blanks and two reagent blank spikes, duplicates of DORM-2 standards and duplicates of 10 samples. In all cases, the concentrations of metals in samples were estimated by interpolation from a four-point calibration curve.

***Limit of detection***

The limit of detection (LOD) for the solution was initially estimated for each analytical batch as 3 times the standard deviation of the three reagent blanks. Sample LODs were then calculated for each metal by multiplying the solution limit of detection by the dilution volume and dividing by the weight of the actual sample. The solution LODs ($\mu g\,mL^{-1}$) are as follows: Pb (0.001), Cd (0.001), Zn (0.002), Mn (0.002), Fe (0.005) and Hg (0.001). The sample LOD ($\mu g\,g^{-1}$) are as follows: Pb (0.025), Cd (0.025), Zn (0.05), Mn (0.05), Fe (0.125) and Hg (0.025).

***Quality assurance and quality control measures***

To ensure the validity of results, the following measures were taken. Prior to sample analysis, certified reference samples (DORM-2) for all metals were analysed in order to verify adequate system performance. Agreement of spectrometer readings with DORM-2 certified reference standards analysed prior to sample analyses and in between 10 sample runs were satisfactory (Table 1). Each batch of sample analysis was prepared to include three reagent blanks in duplicates to control for background contamination and two reagent blank spikes in duplicate to confirm satisfactory metal recovery greater than 90%. In addition, the correlation coefficient ($r^2$) for the calibration curve was required to be greater than 0.995. All samples were analysed in duplicate.

Table 1. Validation of automatic mercury analyzer and flame atomic absorption spectrometer performance with NRCC DORM-2 standards.

| | DORM-2 standards | |
|---|---|---|
| Element | Certified value ($mg\,kg^{-1}$) | Measured value ($mg\,kg^{-1}$) |
| Pb | $0.065 \pm 0.007$ | $0.062 \pm 0.004$ |
| Zn | $25.6 \pm 2.3$ | $25.8 \pm 0.23$ |
| Fe | $142 \pm 10$ | $143 \pm 2.23$ |
| Mn | $3.66 \pm 0.34$ | $3.62 \pm 0.12$ |
| Hg | $4.64 \pm 0.26$ | $4.32 \pm 0.05$ |
| Cd | $0.043 \pm 0.008$ | $0.045 \pm 0.05$ |

***Statistical analysis***

The descriptive statistics (mean and range) and one-way analysis of variance (ANOVA) were conducted using Excel software. A one-way ANOVA statistical procedure was employed in the assessment of variation in metal concentrations among canned tomatoes of the same brand and across canned tomatoes of different brands.

## Results and discussion

The levels of Fe were highest in the series of metals for 6 brands (Table 2). Mean concentration for Zn was higher than that for Cd, Mn, Pb and Hg in five brands. Cd levels were below LOD ($<0.025\,\mu g\,g^{-1}$) for all brands. Also for all brands, concentrations were generally low for Pb and even lower for Hg, with the highest recorded levels for both heavy metals below $1.0\,\mu g\,g^{-1}$ ($0.116 \pm 0.012\,\mu g\,g^{-1}$ for Pb and $0.102 \pm 0.001\,\mu g\,g^{-1}$ for Hg). The results imply that the likelihood of obtaining high Fe dosage from eating food prepared with canned tomato puree from the study area is more apparent than that of Cd.

Analysis of the data on a brand-to-brand basis shows that FT had the highest Zn and Fe concentrations with mean values of $8.52 \pm 0.68\,\mu g\,g^{-1}$ and $58.57 \pm 14.52\,\mu g\,g^{-1}$, respectively. Fe concentration exhibited the largest differences in variability between brands, with mean concentration in FT brand ($58.57 \pm 14.52\,\mu g\,g^{-1}$) being considerably higher than that in PT brand ($1.68 \pm 1.63\,\mu g\,g^{-1}$). FT products recorded the lowest levels for three metals: Mn ($2.62 \pm 0.33\,\mu g\,g^{-1}$), Pb ($0.071 \pm 0.003\,\mu g\,g^{-1}$) and Hg ($0.011 \pm 0.001\,\mu g\,g^{-1}$). By contrast, PT brand recorded the lowest values for Zn ($2.06 \pm 0.623\,\mu g\,g^{-1}$) and Fe ($1.68 \pm 1.63\,\mu g\,g^{-1}$) but the highest level for Mn ($5.75 \pm 0.47\,\mu g\,g^{-1}$). The highest estimated level for Pb ($0.116 \pm 0.012\,\mu g\,g^{-1}$) was recorded in VT brand whereas the highest mean Hg level ($0.102 \pm 0.001\,\mu g\,g^{-1}$) was recorded in NT brand. The difference

Table 2. Concentration of heavy metals ($\mu g\,g^{-1}$) in canned tomatoes (mean and standard deviation).

| Sample | *n* | Zn | Fe | Cd | Mn | Pb | Hg |
|---|---|---|---|---|---|---|---|
| PT | 11 | $2.06 \pm 0.62$ | $1.68 \pm 1.63$ | $<$LOD | $5.75 \pm 0.47$ | $0.073 \pm 0.022$ | $0.035 \pm 0.015$ |
| VT | 5 | $6.44 \pm 2.85$ | $18.13 \pm 5.78$ | $<$LOD | $5.34 \pm 0.30$ | $0.116 \pm 0.012$ | $0.014 \pm 0.001$ |
| LT | 9 | $8.08 \pm 1.61$ | $23.50 \pm 8.37$ | $<$LOD | $4.75 \pm 1.32$ | $0.092 \pm 0.028$ | $0.031 \pm 0.005$ |
| FT | 8 | $8.52 \pm 0.68$ | $58.57 \pm 14.52$ | $<$LOD | $2.62 \pm 0.33$ | $0.071 \pm 0.003$ | $0.011 \pm 0.000$ |
| NT | 10 | $6.10 \pm 1.30$ | $41.04 \pm 19.47$ | $<$LOD | $4.20 \pm 1.65$ | $0.103 \pm 0.011$ | $0.102 \pm 0.001$ |
| OT | 5 | $3.34 \pm 1.67$ | $30.56 \pm 21.15$ | $<$LOD | $3.66 \pm 1.35$ | $0.088 \pm 0.008$ | $0.038 \pm 0.035$ |
| GT | 13 | $6.98 \pm 2.80$ | $22.06 \pm 8.34$ | $<$LOD | $4.37 \pm 1.28$ | $0.075 \pm 0.035$ | $0.046 \pm 0.064$ |

Table 3. Reported (heavy) metal levels ($\mu g\,g^{-1}$) in canned tomato paste.

| N | Zn | Fe | Cd | Mn | Pb | Reference |
|---|---|---|---|---|---|---|
| 10 | N.R. | 5.4–105.3[a] | N.R. | N.R. | N.R. | Al-Khalifa (1997) |
| 4 | 2.54–6.63[a] | 63.11–96.1[a] | 0.511–1.22[a] | 11.5–23.02[a] | < LOD | Melaku (2009) |
| 7 | 7.4[b] | 6.8[b] | N.R. | N.R. | < LOD | Türker and Yüksel (1997) |
| 5 | 3.08[b] | 3.46[b] | 0.04[b] | 4.35[b] | 2.82[b] | Itodo and Itodo (2010) |
| 20 | 6.01[b] | 6.03[b] | 0.31[b] | N.R. | 0.51[b] | Waheed et al. (2003) |
| 5 | 4.03–92[a] | 30.6–219.58[a] | 0.007–0.111[a] | N.R. | 0.02–2.10[a] | David et al. (2008) |

Notes: N.R.: not reported.
[a]Range of mean levels.
[b]Mean levels.

between the highest concentration (VT) and the lowest concentration (FT) for Pb is only 0.045 $\mu g\,g^{-1}$ whereas Hg's highest (NT) and the lowest (FT) concentrations differed by 0.32 $\mu g\,g^{-1}$.

Considering how levels of heavy metals found in this study compare with those in prior studies (Table 3), it is noted that other research groups including those of Al-Khalifa (1997), David et al. (2008), Itodo and Itodo (2010), Melaku (2009), Türker and Yüksel (1997) and Waheed et al. (2003) have independently assessed levels of heavy metals in different brands of canned tomato paste. Although differences exist in the type and the concentration of acid used, the common approach of wet acid digestion followed by FAAS was employed in all studies. Generally, concentrations found in this study are within the range of values reported in these studies with few exceptions. Mean levels for Fe in each of the three reports (Al-Khalifa 1997; David et al. 2008; Melaku 2009) are consistently more than twofold higher than values obtained in this study. Levels of Mn found by Melaku (2009) are at least fourfold higher than levels of Mn estimated in this study. Cd levels in all literature reports are above the LOD in contrast to this study. Observed differences in concentrations suggest variation of metal content with geographical origin.

Levels of Fe in canned tomato paste (5.4–105.3 $\mu g\,g^{-1}$) exceeded that of their corresponding uncanned products (0.1220–0.2870 $\mu g\,g^{-1}$) (Al-Khalifa 1997). Levels of Zn ($6.01 \pm 0.06\,\mu g\,g^{-1}$), Cd ($0.31 \pm 0.01\,\mu g\,g^{-1}$) and Pb ($0.51 \pm 0.01\,\mu g\,g^{-1}$) were higher than the corresponding levels in raw foodstuffs by 5.2 units (Zn), 4.0 units (Cd) and 9.0 units (Pb) (Waheed et al. 2003). Additionally, levels of Zn, Fe, Cd and Pb in tomato paste packaged in plastic cans were at least twofold lower than corresponding levels in metal cans (David et al. 2008). Also, Fe levels in tomato paste packaged in metallic cans increased from $6.8 \pm 1.1\,mg\,kg^{-1}$ to $20.6 \pm 3.7\,mg\,kg^{-1}$ in 73 days of storage (Türker and Yüksel 1997). These observations lead to the suggestion that heavy metal contents may exceed the safety limits when packaged in metallic cans or when stored in metallic cans for long periods. Maximum levels obtained for Fe in FT brand ($58.57 \pm 14.52\,\mu g\,g^{-1}$) in this study attest to this observation.

Levels of Zn can be increased in tomato contaminated from storage in galvanised containers (Henriksen et al. 1985). Pb may find its way into canned tomato from lead piping or casserole vessels used in cooking tomato paste prior to canning. Examples of contamination with Pb from the solder of tin containers are still encountered (Henriksen et al. 1985). Prolonged storage of canned tomatoes may lead to internal corrosion of metallic cans, metallic dissolution and leaking of heavy metal constituents into the canned product (Nincević et al. 2009). Heavy metals may also contaminate processed tomato paste through the addition of preservatives, stabilisers and synthetic colouring agents (Oduoza 1992).

Evaluating the toxicological significance of the data, estimated levels were compared with Codex Standard 193-1995 (Codex 2010): 0.05 $mg\,kg^{-1}$ Cd, 1.0 $mg\,kg^{-1}$ Pb and 0.1 $mg\,kg^{-1}$ Hg and with the WHO/FAO minimum allowable intake data of heavy metals: 30 $mg\,kg^{-1}$ Zn (FAO 1983), 40 $mg\,kg^{-1}$ Fe (WHO 1993), 0.5 $mg\,kg^{-1}$ Cd (FAO 1983), 0.5 $mg\,kg^{-1}$ Pb (FAO 1983) and 0.5 $mg\,kg^{-1}$ Hg (WHO 1993). Levels of Zn, Pb, Hg and Cd obtained in this study are generally low and below the Codex Standard and WHO levels for all brands. Levels of Fe in FT and NT brands were, however, above the WHO/FAO limits of tolerable intake. This observation suggests that the contribution of FT and NT canned tomato paste brands to the daily intake of Fe from food would be substantial. Besides FT and NT brands, consumption of the other brands of canned tomato paste sampled from Kumasi in Ghana may not lead to hazardous effects on human health as estimated values were below the WHO/FAO recommended standard limits.

## Conclusions

Significant differences were observed in heavy metal concentrations across seven different canned tomato brands. Fe had the highest concentration in all the tomato samples with values ranging from $1.68 \pm 1.63\,\mu g\,g^{-1}$ to $58.57 \pm 14.52\,\mu g\,g^{-1}$. Cd levels were below detection limit in all the canned tomato samples. The mean concentrations of Zn ranged from $2.06 \pm 0.62\,\mu g\,g^{-1}$ to $8.52 \pm 0.68\,\mu g\,g^{-1}$, whereas Fe ranged from $1.68 \pm 1.63$ to $58.57 \pm 14.52\,\mu g\,g^{-1}$. Mean levels of Mn, Pb and Hg in the canned tomatoes are in the ranges $2.62 \pm 0.334$ to $5.75 \pm 0.465\,\mu g\,g^{-1}$, $0.07 \pm 0.003$ to $0.116 \pm 0.012\,\mu g\,g^{-1}$ and $0.011 \pm 0.001$ to $0.102 \pm 0.001\,\mu g\,g^{-1}$, respectively. Levels of heavy metals in six brands of canned tomato paste were found to decrease in the following order: Fe > Zn > Mn > Pb > Hg > Cd. The metal concentrations for five brands of canned tomatoes were within the WHO/FAO recommended limits for food.

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