The Pharmaceutical and Chemical Journal, **2016, 3(1):172-177**

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Trace Metals in Food Condiments Processed with Manual Metallic Grinders

Jude C Nnaji, Prosper N Emmanuel

Department of Chemistry, Michael Okpara University of Agriculture, Umudike, P.M.B. 7267 Umuahia, Abia State, Nigeria.

Abstract The study was conducted in order to determine the effect of metallic manual grinding machine on metal concentrations in food condiments. Food condiments (tomato, crayfish, dika nut, melon and pepper) were purchased from three local markets (Ndoro, Ubani and Ahiaeke) and were each divided into two parts. One part of each condiment from a specific market was pulverized with plastic mortar and pestle while the other part was pulverized using manual grinding machine. In all, three different metallic grinders (Corona® brand) were used for the three condiment lots from the three markets. The samples (plastic mortar samples, PMS and metallic grinder samples, MGS) were digested with HNO_3 and aqua regia and analyzed for metals (Fe, Zn, Cr and Ni) using Flame Atomic Absorption Spectrophotometry (FAAS). The results show enrichment of condiment samples with the metals as a result of the use of the metallic grinder for crushing them since metal concentrations were higher in all metallic grinder samples (MGS) compared to plastic mortar samples (PMS). Mean Fe concentrations in PMS for the three condiment lots were significantly lower ($P<0.05$) than mean Fe concentration in MGS indicating substantial Fe enrichment.

Keywords metals, grinder, mortar, condiment

Introduction

Food condiments refer to spices, sauces or food preparations added to food in order to improve flavour or impart a desired flavour [1]. The exact definition of food condiment varies from place to place and it is used interchangeably with the word, seasoning. Condiments are consumed by various ethnic groups in Nigeria and even include fermented meats and fish [2]. Trace metals are common pollutants which are widely distributed in the environment and usually occur in trace amounts [3]. Trace metals are divided into essential and non-essential metals. Basically, essential trace elements are needed for tissue repair, growth, metabolism and for slowing down some degenerative processes [4]. However, both deficiency and excess amounts of these essential trace elements result in serious problems in the human and animal body. Non-essential trace metals are those that may be toxic to organisms. Knowledge of trace metal content in foodstuff is important for the identification of adequate, sub-adequate and marginal intake levels for humans, so that diseases related to trace metals deficiency or over-enrichment can be overcome.

Most developing like Nigeria experience high mortality rate and this is exacerbated by poor health delivery and inadequate monitoring of foodstuffs which results in high intake of unwholesome food. High level of trace metals in food is a potential source of disease when consumed by humans and constant monitoring of foodstuff for trace metal contamination is crucial for the health of the citizenry due to the various diseases they induce. Unhygienic grinding of foodstuff with old and worn out grinding machines is the usual practice in Nigerian markets and the operators do not appreciate the health risks involved in their operations. This study seeks to determine the concentrations of trace metals (Fe, Zn, Cr and Ni) in tomato **(***Solanum lycopersicum L.*), melon (*Citrullus lanatus*), dika nut (*Irvingia gabonensis*), crayfish (*Astacus fluviatilis*) and pepper (*Capsicum annum*) crushed with manual grinders.

Materials and Methods

Sampling and sample pre-treatment

Triplicate samples of the five food condiments; tomato **(***Solanum lycopersicum L.*), melon (*Citrullus lanatus*), dika nut (*Irvingia gabonensis*), crayfish (*Astacus fluviatilis*) and pepper (*Capsicum annum*) were procured from Ndoro (Ikwuano Local Government Area), Ubani and Ahiaeke (Umuahia South Local Government Area) Markets in Abia State. Each condiment type in the three lots was divided into two parts; one part was homogenized with plastic mortar and pestle while the other part was homogenized with manual metallic grinder (Corona® brand). This gave a total of 30 triplicate samples (ten from each market) i.e. 5 plastic mortar samples (PMS) and 5 metallic grinder samples (MGS) in triplicate. The samples were stored in a refrigerator at 4 ^{o}C prior to digestion.

Apparatus, reagents and solvents

All glassware were washed with detergent and rinsed with distilled-deionized water. They were then soaked for 24 h in 10 % nitric acid solution and dried in an oven before use. Analytical grade reagents were used and standard solutions of trace elements were freshly prepared on the day of analysis.

Sample digestion

The samples were digested in triplicate as earlier described [5]. Concentrated HNO_3 (10 ml) was separately added to the plastic mortar and manual grinder samples (5 g each) contained in 250 ml beakers. Each beaker was covered with watch glass for initial reactions to subside. The content of each beaker was then evaporated to dryness. 5 ml of aqua regia was added and the content evaporated to dryness after which 10 ml of 1 M HNO_3 was added and the suspension filtered with Whatman no. 42 filter paper. The filtrate was diluted to volume with distilled-deionized water in a 50 ml volumetric flask and transferred into a sterile plastic bottle which was stored in a refrigerator at 4 ^{o}C prior to analysis [6].

Method of analysis for heavy metals

A total of four metallic elements, Cr, Fe, Ni and Zn were determined in the samples using Buck Scientific Flame Atomic Absorption Spectrophotometer (FAAS) – model 210VP. FAAS determines the concentration of heavy metals at the parts per million (mg/kg) level. A liquid is aspirated and mixed as an aerosol with combustible gasses (acetylene-air or acetylene-nitrous oxide). The mixture is ignited in a flame of temperature ranging from 2100 to 2800 °C. During combustion, the metal of interest contained in sample matrix is atomized. A light beam from the Hollow Cathode Lamp whose cathode is made of the metal being determined passes through the flame into a monochromator and is detected. Free, unexcited ground state atoms of the metal of interest absorb light at characteristic wavelengths. The reduction of light energy at the analytical wavelength is a measure of the amount of the metal present in the sample.

Preparation of standards

Five standard solutions for each element (Fe, Zn, Cr and Ni) were prepared from a stock solution by serial dilution. In this case, stock solutions with a concentration of 1000 ppm were diluted to obtain standard solutions of low concentration. The absorbance obtained from AAS instrument for each standard of a particular element was used in drawing calibration curves.

Method validation

The procedure and method was validated by the use of a standard reference sample. This involved determining the metal concentrations in standard reference food sample from International Atomic Energy Agency (IAEA) obtained through Rofnel Energy Services Ltd, Port-Harcourt. The standard reference material was digested and analyzed with the methods used for the condiment samples. The percentage recovery was calculated using the formula:

$$\% \text{ Recovery} = (\text{ARM}/\text{CRM}) \times 100$$

Where: ARM = analyzed metal concentration in reference standard, CRM = metal concentration indicated on reference standard

Analysis of samples

The standard solutions were aspirated into the AAS and the absorbance recorded. The sample and blank solutions were also aspirated into the AAS instrument (Buck Scientific AAS – model 210VP) and the absorbance recorded. Table 1 shows the analytical conditions used for the AAS instrument.

Table 1: Analytical Conditions for AAS

Metal	Wavelength (Nm)	Silt Width(Nm)	Flame type
Zn	213.9	0.7	A-A
Fe	248.8	0.2	A-A
Ni	232.0	0.2	A-A
Cr	357.9	0.7	A-A

A-A = Air- Acetylene

Calibration curves were drawn for each analyte and the concentration of each trace metal analyzed was determined by extrapolation on the curve.

Conversion of results

Metal concentrations obtained from extrapolation on the calibration curves were in weight/volume basis (mg/L) and were converted to weight/weight basis (mg/kg) using the formular:

$$\text{Conc. (mg/kg)} = \frac{\text{conc. (mg/L)}}{\text{wt of sample digested (g)}} \times \text{dilution factor}$$

$$\text{dilution factor} = 50 = \text{volume (mL) of the digest solution}$$

Data analysis

The data was analyzed using Statistical Software for Social Scientists (SPSS version 20.0) for Windows software package. Mean concentrations and standard deviations were calculated for each parameter. Comparison of means was done with Duncan multiple range test.

Results and Discussion

The percentage recoveries for the various metals in the standard reference materials are presented in Table 2.

Table 2: Percentage recovery values

Parameter	% Recovery
Zinc	84
Fe	90
Ni	87
Cr	88

The percentage recoveries were in the range of 84 – 90 %. The acceptable recovery range is 80–105 %, therefore, the digestion and FAAS methods are reliable.

Table 3: Mean Metal Concentrations in condiment samples of Ndoro Market

Sample ID	Zn (mg/kg)	Ni (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
Cray fish 1	9.50 ±0.30	<0.01	10.00 ±0.80	0.58±0.05
Crayfish 2	10.80 ±1.60	<0.01	16.00 ±2.70	0.93± 0.20
Melon 1	4.30 ±0.10	<0.10	13.30 ±2.00	0.11±0.08
Melon 2	7.80 ±0.30	<0.10	20.52 ±4.80	0.70±0.12
Dika nut 1	6.00 ±0.10	<0.10	26.70 ±4.90	0.33±0.09
Dika nut 2	6.40 ±2.00	<0.10	33.6 ±8.80	0.86±0.27
Pepper 1	2.60 ±0.10	<0.10	2.90 ±0.10	0.20±0.09
Pepper 2	4.20 ±0.90	<0.10	5.10 ±0.90	0.53±0.10
Tomato 1	0.70 ±0.00	<0.10	0.93±0.27	<0.01
Tomato 2	1.10 ±0.08	<0.10	3.30 ±0.10	0.12±0.04

1 = plastic mortar samples, 2 = metallic grinder samples

Table 3 shows the results of FAAS analysis of the metallic grinder and plastic mortar samples for the condiment samples from Ndoro market.

Ni was not detected in any of the samples while Cr was detected in all samples except in the plastic mortar pulverized tomato sample. Ni and Cr concentrations in crayfish have been reported to be 0.11 and 1.08 µg/g, respectively [7]. Zn concentration in plastic mortar pulverized (PMS) and metallic grinder pulverized (MGS) crayfish, dikanut and tomato were similar ($P>0.05$) but Zn concentrations in MGS melon and pepper were significantly higher ($P<0.05$) than concentrations in PMS samples. Fe concentrations in all MGS condiment samples were significantly higher ($P<0.05$) than PMS samples and substantial Fe enrichment resulted from the use of the manual metallic grinder. A study to determine heavy metal contamination of *Lycopersicon esculentum* and *Citrullus lanatus* by different milling techniques and cookwares, concluded that the locally fabricated milling machine added the highest concentration of Fe to the condiments [8]. Though Fe is an essential metal in the human body and is involved in many metabolic processes like oxygen transport by hemoglobin, excessive amounts of Fe can lead to cardiovascular disease [9]. The World Health Organization (WHO) recommended limit for Fe in food is 15 mg/kg [10]. The mean concentrations of Fe in all MGS samples exceeded this value with the exception of pepper and tomato samples.

The values in table 4 are the results of FAAS analysis of the metallic grinder (MGS) and plastic mortar (PMS) samples purchased from Ubani Market. Ni was also, not detected in any sample since concentrations were below the detection limit of the AAS machine. Cr was not detected in plastic mortar pulverized (PMS) melon and tomato samples.

Table 4: Mean Metal Concentrations in condiment samples from Ubani Market

Sample ID	Zn (mg/kg)	Ni (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
Cray fish 1	7.85 ±1.25	<0.01	12.60 ±2.38	0.45±0.07
Crayfish 2	12.01 ±3.22	<0.01	15.94 ±3.10	0.62±0.13
Melon 1	2.90 ±0.81	<0.10	8.77 ±1.65	<0.01
Melon 2	4.36 ±1.05	<0.10	17.53 ±3.60	0.14±0.03
Dika nut 1	5.16 ±1.08	<0.10	18.10 ±3.88	0.28±0.05
Dika nut 2	8.44 ±2.70	<0.10	28.16 ±5.11	0.75±0.07
Pepper 1	2.27 ±0.93	<0.10	3.47 ±1.00	0.11±0.00
Pepper 2	5.16 ±1.37	<0.10	6.22 ±1.86	0.84±0.04
Tomato 1	2.64 ±0.85	<0.10	2.15±0.90	<0.01
Tomato 2	3.80 ±1.02	<0.10	5.65 ±1.20	0.21±0.09

1 = plastic mortar samples, 2 = metallic grinder samples

Table 5: Mean Metal Concentrations in condiment samples from Ahiaeke Market

Sample ID	Zn (mg/kg)	Ni (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
Cray fish 1	5.75 ±1.22	<0.10	6.72 ±1.25	0.28±0.13
Crayfish 2	10.31 ±2.74	<0.10	11.88 ±3.51	0.72±0.18
Melon 1	2.64 ±0.70	<0.10	10.12 ±1.96	0.90±0.01
Melon 2	6.85 ±2.01	<0.10	20.30 ±4.27	0.94±0.02
Dika nut 1	4.91 ±1.31	<0.10	15.39 ±3.14	0.08±0.01
Dika nut 2	6.27 ±1.93	<0.10	24.36 ±5.91	0.13±0.05
Pepper 1	3.51 ±0.85	<0.10	1.78 ±0.29	0.04±0.01
Pepper 2	5.06 ±2.00	<0.10	4.44 ±1.25	0.11±0.05
Tomato 1	1.89 ±0.95	<0.10	3.80±0.94	<0.01
Tomato 2	3.12 ±1.30	<0.10	6.01 ±1.33	<0.01

1 = plastic mortar samples, 2 = metallic grinder samples

However, the results show enrichment of condiment samples with Zn and Fe as a result of the use of the metallic grinder for crushing them since metal concentrations were higher in all metallic grinder samples compared to plastic mortar samples. For instance, mean Zn concentration in MGS-crayfish 1(2.01 ±3.22) was significantly higher

(P<0.05) than that of PMS-crayfish (7.85 ±1.25 mg/kg). Mean Fe concentration in PMS-melon (8.77 ±1.65 mg/kg) was significantly lower (P<0.05) than the value for MGS-melon (17.53 ±3.60 mg/kg) indicating substantial Fe enrichment arising from the use of the manual metallic grinder. This is in accordance with the conclusion that foods processed with locally fabricated mill sometimes incorporates contaminants like heavy metals [11]. Zinc is an essential metal in the human body and is involved in cellular replication, development of the immune response and is a cofactor of over 200 enzymes involved in body metabolism. However, abnormal levels of Zn can be toxic since it interfers with copper metabolism [12-13].

The results of FAAS analysis of the metallic grinder (MGS) and plastic mortar (PMS) samples purchased from Ahiaeke Market is shown in Table 5.

Again, Ni concentrations (in all samples) and Cr concentrations (tomato samples) were below the detection limit of the FAAS. Zn and Fe concentrations in all MGS samples were significantly higher (P<0.05) than concentrations in PMS samples. A study of the uptake of Cu, Fe and Zn by crops including tomato and pepper processed with grinding stone, blender and disc attrition mill concluded that Fe was significantly taken up by the three grinding devices while Cu and Zn significantly taken up by only the disc attrition mill [14].

Conclusions and Recommendations

The results of this study show the enrichment of all the food condiments with Zn and Fe due to the use of old manual metal grinders in crushing them. Ni was not detected in both the metallic grinder and plastic mortar processed samples. Therefore, food condiments pulverized with metallic grinders may be sources of trace metal accumulation in humans who consume condiments. Consumption of metal laden condiments over long periods of time may lead to chronic toxicity even with essential metals like Fe and Zn.

(i) Further research should be carried out on the deposition of other trace metals in food due to the use of metallic grinders

(ii) Considering the health risks associated with the consumption of trace metal contaminated food by the public, it is necessary for Public Health Authorities to monitor the use of metal grinder in food processing.

(iii) The Nigerian Government should monitor the production and importation of grinding machines because it may be a source of trace metal contamination in food.

References

1. Wikipedia. Condiment. https://en.wikipedia.org/wiki/Condiment. Retrieved 25 September 2015
2. Uzogara, S. G., Agu, L. N., & Uzogara, E. O. (1990). A review of traditional fermented foods, condiments and beverages in Nigeria: Their benefits and possible problems. *Ecology of food and nutrition*, *24*(4), 267-288.
3. O'Neil, P. (1993). *Environmental Chemistry*. Chapman and Hall, London, 193.
4. WHO and FAO. *A manual on nutrition, care and support of people living with HIV/AIDS*. World Health Organization, Rome, 2002. Pp 1-50
5. Bamgbose, O., Odukoya, O., & Arowolo, T. O. A. (2000). Earthworms as bio-indicators of metal pollution in dump sites of Abeokuta City, Nigeria. *Revista de biologia tropical*, *48*(1), 229-234.
6. American Chemical Society. Chemistry and biochemistry of agriculture and food along with safety. *Journal of agricultural and food chemistry*, 2007, 55: 5904-5905.
7. Orisakwe, O. E., Mbagwu, H. O., Ajaezi, G. C., Edet, U. W., & Uwana, P. U. (2015). Heavy Metals in Seafood and Farm Produce from Uyo, Nigeria: Levels and health implications. *Sultan Qaboos University medical journal*, *15*(2), e275.
8. Anthony, B. O., Chukwu, C. G., Lawal, O. O., & Osinaike, T. S. Some Nigerian Traditional Food Milling Techniques and Cookware Increase Concentrations of Some Heavy Metals in Lycopersicon Esculentum and Citrullus Lanatus.
9. Lynch, S. R. (1997). Interaction of iron with other nutrients. *Nutrition Reviews*, *55*(4), 102-110.

10. WHO. Toxicological evaluation of certain food additives and food contaminants. *WHO Food series* 18, 2006. World Health Organization, Geneva.
11. Yahaya, D. B., Aremu, D. A., & Abdullahi, I. (2012). Investigation of metal contaminants in locally ground foods (beans and tomatoes). *Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS)*, *3*(1), 339-343.
12. Salgueiro, M. J., Zubillaga, M. B., Lysionek, A. E., Caro, R. A., Weill, R., & Boccio, J. R. (2002). The role of zinc in the growth and development of children. *Nutrition*, *18*(6), 510-519.
13. Uriu-Adams, J. Y., & Keen, C. L. (2005). Copper, oxidative stress, and human health. *Molecular aspects of medicine*, *26*(4), 268-298.
14. Odukoya, O. O., Folarin, M., & Akinnawo O. O. (1993). Uptake of iron, copper and zinc by some selected Nigerian food materials using different grinding methods. *PJST*, 3, 19-23.