Heavy metal contamination of selected spices obtained from Nigeria

GAYA, UI; IKECHUKWU, SA

Department of Pure and Industrial Chemistry, Bayero University Kano, 700241 Kano State, Nigeria
*Correspondence author email: uigaya.chm@buk.edu.ng

ABSTRACT: In this study, the levels of trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Mo, Pb, Zn) in twenty two spices representing four spice groups (seeds, bulbs, leaves, fruit pods and rhizome) from a major market in Northern Nigeria were determined using atomic absorption spectroscopy, and assessed based on regulatory standards. Garlic exhibited the highest zinc concentration (21.733 ±0.044 mg/kg), which falls lower than the upper toxic level for most plants. Lead concentrations peaked in African nutmeg (4.717 ± 0.017 mg/kg) but are lower than the normative for the final dosage form of medicinal plants. The daily intake-based hazard of the spices was assessed using the minimum risk levels set by WHO, and the FAO/WHO maximum tolerable intake limits. All the spices contain excessive cobalt and copper with maximum levels (mg/kg) in ginger cobalt (11.117 ±0.069) and African nutmeg (15.300 ± 0.041), respectively. The estimated daily intake values (µg/kg day) of onion (1.10), ginger (12.00), utazi (1.30), alligator paper (1.20), garlic (0.89), Ashanti leaves (0.88), castor seeds (1.20), and shallot (0.86) were higher than the provisional maximum tolerable intake set by FAO/WHO, constituting a potential risk to human health. These results show that spices can accumulate exceeding levels of toxic metals whose potential risk to human health should be given priority. © JASEM

KEYWORDS: heavy metal; contamination; Nigeria; spices; health; daily intake

Over the millennia, spices have been used in changing world’s cuisine and medicine (Dukes, 2003). Regrettably, significant quantities of heavy metals have been detected in natural food spices such as pepper and mustard (Krejpcio, 2007; Khan et al., 2014). Although low levels of some heavy metals such as chromium, iron, manganese, cobalt, zinc and copper are considered essential, even low levels of other metals such as cadmium and lead can have toxic effects in human biochemical reactions (Jarup, 2003; Cao et al., 2010). The accumulation of these important hazardous metals can breed middle-term or long-term health effects manifesting inter alia as depression, chronic asthma, liver damage, insomnia, kidney damage and neurological disorders (Mandal and Suzuki, 2002; Barakat, 2011).

Generally speaking, Cd, Pb, Cr, Cu, Zn, As and Ni are the most hazardous heavy metals in the environment (Brimer, 2011). Despite being the most ecotoxic metal, lead resides naturally in plants. Recently, Pb and Cd were listed by the Agency for Toxic Substances and Disease Registry (ATSDR, 2015) as second and seventh priority toxic substances. Consequent upon this, it is imperative to monitor the hazardous effect of the heavy metal in common condiments. In a study, Egyptian spices were found to contain alarming levels of Pb, Cd, Cr, Sn, Mn, Zn, Co, Cu, Fe and Ni (Abou-Arab & Abou Donia, 2000).

Admittedly, the extent of contamination of the spices with heavy metal varies from one plant to another. Reasons for this variation have been revealed by the work of Chizzola et al. (2003), which determined the levels of Cd, Fe, Cu, Zn and Pb in spices, aromatic and medicinal plants from different regions of Austria and confirmed that the tendency to accumulate Cd is species dependent while Pb uptake occurs rather by chance.

Nigerians are prone to spicy foods which lends them to the associated consequences. Previously, the levels of Cd, Pb, Cu, Cr, Ni, Fe and Zn have been determined in Nigerian sesame (Obiajunwa et al., 2005) and some Nigerian spices from Warri (Iwegbue et al., 2011). In this study, we investigate various common spices for possible metal (Pb, Cu, Cd, Zn, Cr, Co, Ni, Mo, Fe and Mn) contamination.

MATERIALS AND METHODS
Sample Collection and Preparation: Twenty two different spices were obtained from Yankura, Abubakar Rimi market, Kano metropolis (lat. 11° 30N, long. 8° 38E). The samples were categorized as bulbs, fruit pods, leaves, rhizome or seeds. The scientific name of the plants and the plant part used in the study are listed in Table 1.
Table 1: List of the spices investigated with their groups, and botanical names of the source plants.

| Spice group | Plant        | Botanical name       |
|-------------|--------------|----------------------|
| Bulbs       | Onions       | Allium cepa          |
|             | Shallot      | Allium aggregatum    |
|             | Garlic       | Allium sativum       |
| Rhizome     | Ginger       | Zingiber officinale  |
| Seeds       | Alligator Pepper | Aframomum melegueta |
|             | Cloves       | Syzygium aromaticum  |
|             | African nutmeg | Monodora myristica  |
|             | Ashanti Pepper | Piper guineense      |
|             | Efu          | Monodoro Sp          |
|             | African locust bean | Parkia biglobosa |
|             | Melon        | Coriaceae lanatus    |
|             | Castor seed  | Ricinus communis     |
|             | Nutmeg       | Myristica fragrans   |
| Leaves      | Uziza        | Piper guineense      |
|             | Curry        | Murrya koenigii      |
|             | Scent leaves | Ocimum gratissimum   |
|             | Utazi        | Gongronema latifolium|
|             | Bay leaves   | Lauras nobilis       |
| Fruit pods  | Red chili pepper | Capsicum annum     |
|             | Yellow pepper | Capsicum annum       |
|             | Red bell pepper | Capsicum annum     |
|             | African pepper | Xylopia aethiopica  |

In order to ensure that metals determined are exclusively those uptaken by the plants, each sample was thoroughly washed with tap water and then with deionized water. The samples were then dried in air, followed by oven drying at 80 °C until constant weight. The dry samples were ground to fine particle and stored in airtight nylons.

Sample Preparation and Digestion: Metal extraction was accomplished by the wet digestion. Exactly 1 g of dry spice powder was weighed into 250 cm³ beakers, mixed with 20 cm³ of 2:1 HNO₃/HClO₄ and heated in a fume cupboard for 5-10 min using hot plate. Completion of digestion was marked by the evolution of white fumes. The digests were allowed to cool, diluted with deionized water (to avoid chemical attack of filter paper), then filtered into 50 cm³ standard volumetric flask and made up to the mark with the deionized water. Calibration standards as well as blank were prepared at the same time as the samples. All standards were prepared from nitrates (in concentrations of 0.01, 0.2, 0.4, 0.6, 0.8, and 1 mg/dm³) except for molybdenum and manganese which were prepared from (NH₄)₂MoO₄·4H₂O and MnCl₂, respectively.

Heavy Metal Determination: The filtrate resulting from wet digestion was subsequently analyzed for Pb, Cu, Fe, Cd, Zn, Cr, Co, Ni, Mo, and Mn using Hitachi Z-5000 flame atomic absorption spectrophotometer(AAS). The AAS was fueled by acetylene. Standards were analyzed accordingly but devoid of the spice. Chromium was determined in the +3 oxidation state and the standard used was Cr(NO₃)₃·9H₂O. The actual concentrations were extrapolated from calibration curves. Analytical concentrations in mg/dm³ were converted to mg/kg. Each analysis was repeated twice and standard deviations from the mean values were calculated.

Human Health Risk Assessment: The health risk associated with the consumption of the spices under study was estimated based on daily intake as estimated daily intake (EDI). This parameter was calculated on the uniform basis of 10 g raw spice per 60 kg body weight.

\[
EDI = \frac{(C \times AC) \times bw}{Cw}
\]

C (mg/kg) is the concentration of heavy metals in the raw spice, AC is the average dry weight of the spice consumed by local inhabitants based on g day⁻¹ person⁻¹ and bw is the average adult body weight (60g).

Quality Control: The method of AAS analysis was validated by recovery method. Samples of onions, melon, garlic, scent leaves and African pepper were spiked with Fe, Cu, Mn, Zn, and Mo doses, respectively. In a typical recovery test, exactly 1 mg/dm³ of the metal was added to 1g of each of the samples in a 250 cm³ beaker and digested with 20 cm³ 2:1 HNO₃/HClO₄. The digest was treated as described above. Percentage recovery was calculated using the relation:

\[
\text{Recovery (\%)} = \frac{\text{Amount determined}}{\text{Amount added}} \times 100
\]

*GAYA, UI; IKECHUKWU, SA
The results of the recovery of spikes of Fe, Cu, Mn, Zn, and Mo from onions, melon, garlic, scent leaves and African pepper, which were 90%, 89%, 90%, 95% and 97% respectively, which validates the method and assures its quality (Table 2). In other words all the metal recoveries are within 11% of the true concentrations, thus attesting the suitability of the AAS method.

| Metals | Spice sample (g) | Initial conc. (mg/kg) | Final conc. (mg/kg) | Amount recovered | Recovery (%) |
|--------|------------------|-----------------------|--------------------|-----------------|--------------|
| Fe     | Onion            | 275.90                | 280.65             | 0.90            | 90           |
| Cu     | Melon seed       | 2.00                  | 6.01               | 0.89            | 89           |
| Mn     | Garlic           | 2.28                  | 6.78               | 0.90            | 90           |
| Zn     | Scent leaves     | 8.88                  | 13.65              | 0.95            | 95           |
| Mo     | African pepper   | 7.67                  | 12.55              | 0.97            | 97           |

**RESULTS AND DISCUSSION**

**Assessment of Heavy Metals:** The results of heavy metal analysis are presented according to the spice group (seeds, bulbs, leaves, fruit pods and rhizome; Tables 3-7).

| Spices          | Statistics | Cd    | Cr     | Cu     | Co     | Fe     | Mn     | Ni     | Mo     | Pb     | Zn     |
|-----------------|------------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Castor          | Mean       | 7.800 | 3.150  | 9.450  | 10.550 | 16.667 | 3.750  | 2.733  | 3.233  | 2.700  | 13.050 |
|                 | SD         | 0.054 | 0.010  | 0.027  | 0.019  | 0.084  | 0.025  | 0.014  | 0.033  | 0.011  | 0.022  |
| Baobab          | Mean       | 3.200 | 4.067  | 8.100  | 7.217  | 9.733  | 5.000  | 4.100  | 3.783  | 3.433  | 13.050 |
|                 | SD         | 0.021 | 0.011  | 0.027  | 0.020  | 0.048  | 0.043  | 0.014  | 0.018  | 0.023  | 0.022  |
| Efu             | Mean       | 3.550 | 4.383  | 9.450  | 9.433  | 13.883 | 5.833  | 3.883  | 4.300  | 3.250  | 14.867 |
|                 | SD         | 0.012 | 0.011  | 0.027  | 0.051  | 0.048  | 0.014  | 0.021  | 0.049  | 0.022  | 0.045  |
| Ashanti pepper  | Mean       | 4.250 | 3.150  | 7.200  | 9.433  | 18.067 | 6.667  | 4.117  | 6.983  | 2.517  | 14.500 |
|                 | SD         | 0.021 | 0.010  | 0.041  | 0.051  | 0.096  | 0.029  | 0.015  | 0.018  | 0.006  | 0.012  |
| Cloves          | Mean       | 3.550 | 2.830  | 9.450  | 8.333  | 20.833 | 8.333  | 3.417  | 5.383  | 3.800  | 13.050 |
|                 | SD         | 0.012 | 0.019  | 0.027  | 0.034  | 0.084  | 0.052  | 0.014  | 0.049  | 0.011  | 0.038  |
| Melon           | Mean       | 4.250 | 4.030  | 9.000  | 7.217  | 18.050 | 7.083  | 3.700  | 2.700  | 3.250  | 3.250  |
|                 | SD         | 0.021 | 0.029  | 0.041  | 0.051  | 0.048  | 0.014  | 0.010  | 0.019  | 0.022  | 0.022  |
| African Pepper  | Mean       | 6.383 | 3.450  | 7.650  | 5.567  | 19.450 | 4.167  | 2.283  | 5.383  | 3.983  | 2.533  |
|                 | SD         | 0.022 | 0.010  | 0.016  | 0.051  | 0.048  | 0.014  | 0.008  | 0.049  | 0.006  | 0.033  |
| African Nutmeg  | Mean       | 3.900 | 3.150  | 15.300 | 6.667  | 13.900 | 6.667  | 2.733  | 5.383  | 4.717  | 14.867 |
|                 | SD         | 0.012 | 0.010  | 0.041  | 0.034  | 0.127  | 0.038  | 0.014  | 0.037  | 0.017  | 0.025  |
| Alligator pepper| Mean       | 7.083 | 3.760  | 8.100  | 8.333  | 19.433 | 6.250  | 2.733  | 7.000  | 3.067  | 3.250  |
|                 | SD         | 0.044 | 0.019  | 0.027  | 0.034  | 0.096  | 0.066  | 0.014  | 0.049  | 0.017  | 0.022  |
| Nutmeg          | Mean       | 4.250 | 3.760  | 9.900  | 10.000 | 18.050 | 5.000  | 2.717  | 6.983  | 3.800  | 3.250  |
|                 | SD         | 0.021 | 0.019  | 0.031  | 0.033  | 0.127  | 0.025  | 0.024  | 0.018  | 0.011  | 0.022  |

Minimum values:
- 3.200
- 3.150
- 4.030
- 7.083
- 3.760 + 0.021
- 15.300 + 0.127

Maximum values:
- 7.800
- 4.383
- 15.300
- 7.083
- 4.383 + 0.004
Table 4: Heavy metal concentration (mg/kg) in bulbs

| Bulbs     | Cd    | Cr    | Cu    | Co    | Fe    | Mn    | Ni    | Mo    | Pb    | Zn    |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Garlic    | 5.317±0.022 | 3.450±0.010 | 10.350±0.031 | 13.333±0.067 | 12.500±0.083 | 6.250±0.025 | 4.100±0.014 | 5.383±0.018 | 5.083±0.017 | 21.733±0.044 |
| Onion     | 6.383±0.022 | 5.650±0.019 | 9.450±0.027 | 8.333±0.034 | 10.550±0.145 | 5.833±0.038 | 3.650±0.021 | 5.383±0.037 | 4.167±0.006 | 2.883±0.013 |
| Shallot   | 5.317±0.022 | 3.767±0.019 | 7.200±0.016 | 5.000±0.033 | 13.900±0.127 | 5.833±0.014 | 3.633±0.008 | 4.850±0.032 | 3.250±0.011 | 3.250±0.022 |

Table 5: Heavy metals concentration (mg/kg) in leaves

| Leaves    | Cd    | Cr    | Cu    | Co    | Fe    | Mn    | Ni    | Mo    | Pb    | Zn    |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Bay leaves| 4.967±0.044 | 2.683±0.006 | 12.150±0.027 | 7.783±0.051 | 12.333±0.083 | 5.417±0.058 | 2.733±0.014 | 4.850±0.032 | 3.433±0.006 | 12.317±0.034 |
| Curry leaves| 4.250±0.021 | 2.533±0.011 | 8.550±0.041 | 7.783±0.020 | 12.500±0.083 | 4.583±0.014 | 2.733±0.010 | 3.733±0.050 | 3.617±0.013 | 14.500±0.012 |
| Uziza leaves| 5.317±0.022 | 3.767±0.019 | 9.900±0.041 | 6.117±0.039 | 13.883±0.048 | 5.833±0.038 | 3.233±0.008 | 4.300±0.049 | 3.250±0.011 | 3.250±0.022 |
| Scent leaves| 7.450±0.021 | 5.650±0.019 | 12.000±0.027 | 9.453±0.019 | 20.833±0.144 | 6.250±0.025 | 2.733±0.014 | 4.300±0.049 | 2.883±0.006 | 2.883±0.013 |
| Utazi leaves| 5.317±0.022 | 2.533±0.011 | 9.900±0.041 | 8.333±0.034 | 12.500±0.083 | 6.250±0.025 | 4.333±0.008 | 6.450±0.032 | 4.167±0.017 | 2.167±0.022 |

Table 6: Heavy metals concentration (mg/kg) in fruit pods

| Fruit pod | Cd    | Cr    | Cu    | Co    | Fe    | Mn    | Ni    | Mo    | Pb    | Zn    |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Red bell pepper | 6.033±0.013 | 4.700±0.019 | 12.150±0.011 | 5.550±0.019 | 13.900±0.127 | 5.000±0.050 | 3.417±0.014 | 3.783±0.018 | 4.717±0.023 | 3.983±0.013 |
| Red pepper chili | 5.317±0.022 | 3.767±0.019 | 11.700±0.041 | 7.217±0.020 | 16.667±0.084 | 5.833±0.029 | 2.050±0.014 | 5.383±0.049 | 3.617±0.023 | 3.250±0.022 |
| Yellow pepper | 4.600±0.024 | 4.700±0.019 | 18.100±0.027 | 5.567±0.051 | 13.883±0.048 | 6.250±0.025 | 4.333±0.008 | 5.383±0.049 | 3.357±0.006 | 2.517±0.013 |

Table 7: Heavy metals concentration (mg/kg) in rhizome

| Rhizome | Cd    | Cr    | Cu    | Co    | Fe    | Mn    | Ni    | Mo    | Pb    | Zn    |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ginger  | 7.450±0.021 | 5.650±0.019 | 13.500±0.027 | 11.117±0.069 | 16.667±0.084 | 5.000±0.043 | 3.417±0.014 | 5.383±0.049 | 2.700±0.011 | 10.133±0.02 |

*GAYA, UI; IKECHUKWU, SA
The levels of Cd, Zn, Ni, Mn, Cu, Pb, Fe, Cr, Co, Mo in seeds and their descriptive statistical parameters are shown in Table 3. Cadmium ranged from 3.200 ± 0.021 in baobab seeds to 7.800 ± 0.054 mg/kg in castor seeds. Even the lower limit of the range is above the value set for foods or products by the most regulatory bodies. A maximum permissible limit of 1 mg/kg was prescribed by the FAO/WHO (2002) for food additives. Threshold values (mg/kg) for cereal grains, leafy vegetables and fruiting vegetables are 0.1, 0.2 and 0.05 (FAO/WHO, 2012). Differently, a value of 0.03 mg/kg was prescribed by (WHO, 1999a) for medicinal plants in their final dosage form. The level of Cd in the bulbs, leaves, fruit pods and rhizome are displayed in Table 4, 5, 6 and 7. The tables show that all Cd values are evidently above the FAO/WHO limits. The high levels of Cd may not be unconnected with the agricultural practice, the plant and the soil properties (such as calcereous nature of soil) that affect uptake of the metal (Kabata-Pendas, 2011). A few decades back, McGrath (1993) has reported variability in Cd content (mg/kg) with plant, showing ranges of < 0.1 and 0.4 in beans, 0.9 and 8.2 in carrot and 3.6 and 91.

The mean levels of manganese (mg/kg) in the seeds (Table 3) ranged from 3.750 ± 0.025 in castor seeds to 8.333 ± 0.052 in cloves. The normative limit for Mn in foods has yet to be exactly specified due to non-toxicity of the metal (WHO, 1999b). In fact, plant foodstuff may contain up to 113 mg/kg of this metal (WHO, 1999a). Various medicinal plants of leaves and rhizome (Table 7) records the highest level of this metal (5.650 ± 0.019 mg/kg). Generally, the accumulation of chromium in edible plants may constitute hazard to animals (Oliveira, 2012). In short, investigation has shown the possibility of phytotoxic effect as chromium levels exceed 1 mg/kg (Kabata-Pendas, 2011), which clearly shows possible Cr hazard with consumption of the spices.

The mean concentration of Cu in the spice seeds ranged from 7.200 ± 0.041 mg/kg in Ashanti pepper to 15.300 ± 0.041 mg/kg in African nutmeg (Table 3). These levels of Cu exceed the maximum acceptable daily limit of the metal in crude (fatty) foods (0.4 mg/kg) (FAO/WHO, 2012). The levels of this heavy metal in other spice groups such as bulbs, leaves, fruit pods and rhizome are displayed in Tables 4 to 7. Generally, as adjudged by the joint FAO/WHO standards (FAO/WHO, 2012), all the spices contain excessive copper levels. It is not however surprising as the mean Cu levels (mg/kg) in Egyptian chamomile and saffron were found to contain Cu levels within the same ranges (8.88 ± 1.38 and 11.3 ± 2.4, respectively) (Abou-Arab & Abou Donia, 2000). The mean concentration of iron in the seed samples ranged from 9.733 ± 0.048 mg/kg in baobab seeds to 20.833 ± 0.084 mg/kg in cloves (Table 3). The values of this metal in bulbs, leaves, fruit pods and rhizome (Table 4-7) are also within the same bracket. In actual fact, several workers have shown that natural Fe content of plants can reach orders of 1000 mg/kg (WHO, 1999a). Various medicinal plants of leaves and herbs category from a number of regions of Austria have been reported to contain levels of iron well above 1000 mg/kg (Chizzola et al., 2003).
There has been a dramatic increase in the use of Zn-based fertilizers and addition of sludge to the soil under plants, so it is important to monitor the zinc levels in spices. In this study, zinc levels in seeds group ranged from 2.533 ± 0.033 in African pepper to 14.867 ± 0.045 in efu (Table 3). The highest Zn content (mg/kg) was obtained in garlic 21.733 ±0.044 (Table 4). Among leaves group, curry leaves have the highest zinc content (14.500 ± 0.012 mg/kg; Table 5). For a high number of plants the upper toxic level of zinc is 100 to 500 mg/kg (Kabata-Pendias, 2011) which indicates that all the zinc values determined are within tolerable limits.

Molybdenum is an essential constituent of many enzymes. Molybdenum concentration in the seeds group (mg/kg) ranged from 2.700 ±0.019 in watermelon to 7.000 ±0.049 in alligator pepper (Table 3). Curry leaves had the lowest molybdenum content (3.733 ±0.050 mg/kg) where as utazi leaves accumulated the largest amount of this metal (6.450 ±0.032; Table 5). Ginger contains 5.383±0.049 mg Mo/kg (Table 7). The molybdenum concentrations of bulbs and fruit pods are close to those of the leaves and seeds groups. All the values of Mo determined in this study are below the threshold of 10 mg/kg above which most grazing animals encounter serious problems (Kabata-Pendias, 2011).

In the seeds group, cobalt concentrations (mg/kg) ranged from 6.667 ±0.034 in African nutmeg to 10.550 ±0.019 in cloves (Table 3) while in the bulbs the levels of this metal ranged from 5.000 ± 0.033 in shallot to 13.333 ± 0.067 in garlic (Table 4). In leaves, the cobalt concentration ranged from 6.117 ± 0.039 in uziza to 9.453 ± 0.019 in scent leaves (Table 5). On the other hand, cobalt in fruit pods ranged from 7.217 ± 0.020 in red chili pepper to 9.450 ± 0.027 in red bell pepper (Table 6). Ginger accumulated 11.117±0.069 mg/kg of cobalt (Table 7). The symptoms of phytotoxicity of cobalt become obvious as concentration (mg/kg) ranges between 30 and 40, and hazard to animals is likely when concentrations exceed 60 mg/kg (Kabata-Pendias, 2011). Cobalt is an essential trace element being a component of vitamin $B_{12}$ precursor and applicable in treatment of anemic patients (ATSDR, 2004). Therefore, the levels of cobalt determined in all the spice groups may not represent any potential risk.

**Human Health Risk:** The estimated daily intake (EDI) values of all the heavy metals are displayed in Table 8. The EDI levels of Cu and Pb in all the spices were lower than the provisional maximum tolerable intake (PMTDI)of 0.5 mg/kg day and 0.02 - 3 µg/kg day set by the joint FAO/WHO committee (FAO/WHO, 2012). Because Zn is an essential trace element and absorption depends on some other dietary factors (with average intake of 20 mg/day), the lower limit of the joint FAO/WHO standard (0.3-1 mg/kg bw) (FAO/WHO, 2012) is often exceeded. In fact, some elemental body formulas contain at least 30 mg Fe per capsule. The EDI values of cadmium for most of the spices was lower than the PMTDI for this metal (0.8µg/kg day) (FAO/WHO, 2012). However, were faced with intolerable EDI values of cadmium, associated with the consumption of onion, ginger, utazi, alligator paper, garlic, Ashanti leaves, castor seeds, and shallot.

As seen from Table 8, cobalt levels in all the spices is above the minimal risk levels for oral intake (MRLOI) (0.01 mg/kg day) recommended by ATSDR (ATSDR, 2016). Similarly, copper levels exceed the risk levels of 0.005 mg/kg day WHO (1996), meaning potential health risk for the consumers. Zinc with MRLOI of 0.3 mg/kg day, represents some risk in all the spices except in ginger, locust beans, African nutmeg, cloves, efu, melon seeds, bay leaves and castor seeds. Even though Cr in all the spices has exceeded the prescribed MRLOI of 0.1 µg/kg day (ATSDR, 2016), tolerable Cr level could be up to 250 µg/day (WHO, 1996). Because the risk level of Mo is 0.14 to 0.20 mg/kg bw (WHO, 1996), adverse effects are therefore likely to occur with consumption of all the spices except for nutmeg, alligator pepper and utazi. The Ni levels in all the spices are below the WHO permissible limit of 600 µg/day (WHO, 1996), which confirms their safety as food materials.
Table 8: Estimated daily intake of each metal (µg/kg day)

| Spices         | Cr | Cu | Co | Fe | Mn | Ni | Mo | Pb | Zn | Cd |
|----------------|----|----|----|----|----|----|----|----|----|----|
| Ginger         | 0.94| 2.3| 1.9| 2.8| 0.83| 0.57| 0.90| 0.45| 0.17| 12 |
| Onion          | 0.94| 1.6| 1.4| 1.8| 0.97| 0.61| 0.89| 0.70| 0.48| 1.1|
| Garlic         | 0.57| 1.7| 2.2| 2.1| 0.10| 0.68| 0.90| 0.85| 0.36| 0.89|
| Nutmeg         | 0.63| 1.7| 1.7| 3.0| 0.83| 0.45| 0.12| 0.63| 0.54| 0.71|
| Locust Beans   | 0.68| 1.4| 1.2| 1.6| 0.83| 0.68| 0.63| 0.57| 0.22| 0.53|
| African nutmeg | 0.53| 2.6| 1.1| 2.3| 0.11| 0.46| 0.89| 0.79| 0.25| 0.65|
| Alligator pepper| 0.63| 1.4| 1.4| 3.2| 0.10| 0.46| 0.12| 0.51| 0.54| 1.2 |
| Cloves         | 0.47| 1.6| 1.4| 3.5| 0.14| 0.57| 0.90| 0.63| 0.22| 0.59|
| Ashanti pepper | 0.53| 1.2| 1.6| 3.1| 0.11| 0.69| 1.1 | 0.42| 2.4 | 0.71 |
| Efu            | 0.73| 1.6| 1.6| 2.3| 0.97| 0.65| 0.72| 0.54| 0.25| 0.49|
| Ashanti leaves | 0.63| 1.7| 1.0| 2.3| 0.97| 0.54| 0.71| 0.24| 0.54| 0.88|
| Melon          | 0.67| 1.5| 1.2| 3.0| 0.11| 0.62| 0.45| 0.42| 0.24| 0.70|
| Curry leaves   | 0.42| 1.4| 1.3| 2.1| 0.76| 0.46| 0.62| 0.60| 0.17| 0.82|
| Utazi          | 0.42| 1.7| 1.4| 2.1| 0.11| 0.72| 0.12| 0.70| 0.36| 1.3 |
| Bay leaves     | 0.45| 2.0| 1.3| 2.1| 0.90| 0.46| 0.81| 0.57| 0.21| 0.88|
| Castor seed    | 0.53| 1.6| 1.8| 2.8| 0.63| 0.46| 0.54| 0.45| 0.12| 1.2 |
| Shallot        | 0.63| 1.2| 8.3| 2.3| 0.97| 0.61| 0.81| 0.50| 0.54| 0.86|
| Scent leaves   | 0.94| 2.0| 1.6| 3.4| 0.10| 0.46| 0.72| 0.48| 0.48| 0.77|
| Red chili pepper| 0.63| 1.9| 1.2| 2.8| 0.97| 0.34| 0.89| 0.60| 0.40| 0.10|
| Yellow pepper  | 0.78| 1.4| 9.2| 2.3| 0.10| 0.72| 0.78| 0.51| 0.42| 0.60|
| Red bell pepper| 0.78| 2.0| 9.3| 2.3| 0.83| 0.57| 0.63| 0.79| 0.67| 0.31|
| African pepper | 0.58| 1.3| 9.3| 3.2| 0.70| 0.38| 0.75| 0.66| 0.42| 0.12|

Conclusion: The levels of Cd, Cr, Cu, Co, Fe, Mn, Ni, Mo, Pb, Zn in a spectrum of Nigerian spices was successfully determined using AAS and the health risk associated with intake of these heavy metals has been assessed. The accumulation of heavy metals by spice groups followed the order seeds>leaves>bulb>rhizome>fruit pods. For all the spices investigated, cobalt and copper levels have exceeded the risk levels set by regulatory agencies. African nutmeg contains the highest copper concentration, 15.300 ± 0.041 mg/kg, while ginger contains the highest cobalt value 11.117±0.069 mg/kg. The cadmium hazard was associated with only a few species, and cuts the cross-section of the groups.

Acknowledgement: The authors are grateful to Mal. Muhammed Musa of Research Laboratory, Department of Pure and Industrial Chemistry for his assistance to SA. Ikechukwu.

REFERENCES
Abou-Arab, AAK; Abou Donia, MA (2000). Heavy metals in Egyptian spices and medicinal plants and the effect of processing on their levels J. Agric. Food Chem. 48(6): 2300-2304.

ATSDR (2004). Agency for Toxic Substances and Disease Registry (ATSDR) Public Health Statement for Cobalt, Retrieved from http://www.atsdr.cdc.gov/PHS/PHS.asp?id=371 &tid=64 on 6th April, 2016.

*GAYA, UI; IKECHUKWU, SA
ATSDR (2015). Substance Priority List, Agency for toxic substances and disease registry. Retrieved from http://www.atsdr.cdc.gov/spl/ on 28th April, 2016.

ATSDR(2016) Minimal risk levels Agency for Toxic Substances and Disease Registry (ATSDR) Retrieved from http://www.atsdr.cdc.gov/mrls/mrllist.asp#17tag on 11th April, 2016.

Barakat, MA(2011). New trends in removing heavy metals from industrial waste water Arabian J. Chem. 4: 361-377.

Brimer, L (2011). Chemical food safety CAB International, United Kingdom.

Cao, H; Chen, J; Zhang, J; Zhang, H; Qiao, L; Men, Y (2010). Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. J. Environ. Sci. 22: 1792–1799.

Chizzola, R; Michitsch, H; Franz, C (2003) Monitoring of metallic micronutrients and heavy metals in herbs spices and medicinal plants from Austria, Eur. Food Res. Technol. 216: 407–411.

Dukes, JA(2003)CRC Handbook of medicinal spices CRC press, Washington.

FAO/WHO (2002) Limit test for heavy metals in food additive specifications. Explanatory note. Joint FAO/WHO Expert Committee on Food Additives (JECFA).

FAO/WHO (2012). Working document for information and use in discussions related to contaminants and toxins in the GSCTFF. Joint FAO/WHO food standards Programme, CODEX committee on contaminants in foods, Sixth Session, Maastricht, The Netherlands.

Iwegbue, CMA; Overah, CL; Ebigwai, JK; Nwozo, SO; Nwajei, GE; Eguavoen, O (2011). Heavy metal contamination of some vegetables and spices in Nigeria, Int. J. Biol. Chem. Sci. 5(2): 766-773.

Järup, L (2003). Hazards of heavy metal contamination, British Medical Bulletin 68: 167-182.

Kabata-Pendias, A (2011). Trace elements in soil and plants. 4th ed. CRC Press Book

Khan, N; Choi, JY; Nho, EY; Jamila, N; Habte, G; Hong, JH; Hwang, IM; Kim, KS (2014). Determination of minor and trace elements in aromatic spices by micro-wave assisted digestion and inductively coupled plasma-mass spectrometry. Food Chem. 158: 200–206.

Krejpecio, Z; Król E; Sionkowski, S (2007). Evaluation of heavy metals contents in spices and herbs available on the Polish market. Pol. J. Environ. Stud., 16: 97-100.

Mandal, BK; Suzuki, KT (2002). Arsenic round the world: a review. Talanta. 58: 201–235.

Mandiwana, KL; Panichev, N; Resane, T (2006). Electro thermal atomic absorption determination of total and hexavalent chromium in atmospheric aerosols J. Hazard. Mater. B 136: 379–382.

McGrath, SP (1993). Soil quality in relation to agricultural uses, in integrated soil and sediment research: A Basis for Proper Protection. In: Eijsackers, H. J. P. and T. Hamers, eds., Kluwer Academic, the Netherlands.

Mertz, W(1993). Chromium in human nutrition: A review. J. Nutr. 626-633.

Michalski, R (2004). Ion chromatography method for the determination of trace levels of Chromium (VI) in water. Pol. J. Environ. Stud. 13(1): 73-77.

Obajuunwa, EI; Adebiyi, FM; Omode, PE (2005). Determination of essential minerals and trace elements in Nigerian sesame seeds, using TXRF technique. Pak. J. Nutr. 4(6): 393-395.

Oliveira, H (2012). Chromium as an environmental pollutant: Insights on induced plant Toxicity. J. Bot. 375843: 1-8.

WHO (1996). Trace elements in Human Nutrition and Health, WHO, Geneva.

WHO(1999a). Monographs on selected medicinal plants, vol. 1, World Health Organisation (WHO), Geneva.

WHO (1999b) Trace elements in human nutrition and health, World Health Organization

WHO (2008). Guidelines for drinking-water quality, 3rd ed., World Health Organization.