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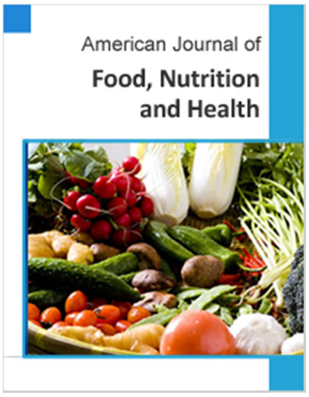

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Trace Metal Contamination of Some Edible Oils Consumed in Benue and Taraba States of Nigeria

Odoh Raphael*, Oko Odiba John, Udegbunam Ifeoma Sandra

Department of Chemical Sciences, Federal University Wukari, Wukari, Nigeria

Email address
odoh@fuwukari.edu.ng (O. Raphael)
*Corresponding author

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Abstract
The determination of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn contents in edible oils (palm oil, ground-nut oil and soya bean oil) bought from various markets of Benue and Taraba state were carried out with Flame Atomic Absorption spectrophotometric technique. The method 3031 developed acid digestion of Oils for metal analysis by Atomic Absorption or ICP spectrometry was used in the preparation of the edible oil samples for the determination of total metal content in this study. The overall results (µg/g) in palm oil sample ranged from 0.028-0.076, 0.035-0.092, 1.011-1.955, 2.101-4.892, 0.666-0.922, 0.054-0.095, 0.031-0.068 and 1.987-2.971 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively, while In ground-nut oil the overall results ranged from 0.011-0.042, 0.011-0.052, 0.133-0.788, 1.789-2.511, 0.078-0.765, 0.045-0.092, 0.011-0.028 and 1.098-1.997 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively. Of the heavy metals considered Cd and Ni showed the highest contamination in the soya bean oil sample. The overall results in soya bean oil samples ranged from 0.011-0.015, 0.017-0.032, 0.453-0.987, 1.789-2.511, 0.089-0.321, 0.011-0.016, 0.012-0.065 and 1.011-1.997 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively. The concentration of Pb was the highest. The degree of contamination by each metal was estimated by the transfer factor. The transfer factors obtained for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in edible oils (palm oil, ground-nut oil and soya bean oil) were 10.800, 16.500, 16.000, 18.813, 15.115, 14.230, 23.000 and 9.418 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in palm oil, and 7.000, 12.500, 8.880, 11.333, 7.708, 10.833, 15.00 and 6.608 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in ground-nut oil while for soya bean oil the transfer factors were 13.000, 11.000, 7.642, 11.578, 4.486, 13.00, 12.333 and 4.412 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively. The inter-element correlation was found among metals in edible oil samples using Pearson's correlation co-efficient. There were positive and negative correlations among the metals determined. All Metals determined showed degree of contamination but concentrations lower than the USP specification.

1. Introduction

The presence of small amounts of trace metals in oils and fats is known to produce deleterious effects on quality. The strongest and most notable proxidants are copper and iron, which produce a noticeable oxidative effect at concentrations as low as 0.005ppm and 0.03 ppm respectively [1-3]. Some metals e.g., nickel, zinc, copper, cadmium and lead are important from a health and safety stand point, as linked either directly or indirectly via cholesterol levels to coronary heart disease [4, 5]. Heavy metal poisoning is a medical condition caused by increased levels of the heavy metals such as Pb, Cd, Cr, Cu, Mn, Ni, and Zn in the body. Although some metals are essential for life, all metals are toxic at sufficiently high concentrations. Generally the gap between what could be described as essential and toxic is very narrow. This is because many biological systems exist naturally on the margin of metal toxicity while the physical and geochemical redistribution of toxic metals in environments or food items by human activities has a strong potential to disrupt ecosystem and food chains [6]. The determination of the inorganic profile of edible oils is important because of the metabolic role of some elements in the human organism. On the one hand there is knowledge of the food's nutritional value which refers to major and minor elements. On the other hand, there is the concern to verify that the food does not contain some minerals in quantities toxic for the health of the consumers, regardless whether this presence of minerals is naturally occurring or is due to contamination during the production processes [7, 8]. Oil characterization is the basis for further nutritional and food technological investigations such as adulteration detection. Edible oil is rich in antioxidant vitamins, trace elements and supplies fatty acids essential for proper growth, development and for general well-being [9, 10]. It has been reported that contamination of diets including edible oil with heavy metals could result from different sources such as drinking water, high ambient air concentrations, industrial waste, acidic rain breaking down soils and food chain. Contamination of the food chain with heavy metals could pose potential health risk to humans and animals because these heavy metals have the ability to "bio-accumulate". Reports from previous research have shown that compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted [11, 12]. Although edible oil remain vital in human nutrition and medicinal treatment, there is concern about its contamination by toxic elements and the potential risk such contamination could pose to the consumers in our locality [13]. This contamination could have access to the oils during planting, harvesting, processing, packaging, storage or sale of the product. Furthermore, studies have indicated that edible oils are often adulterated to mask their colours and properties hence the need to assess the extent of adulteration [14, 15]. It has been shown that edible oil obtained from the fruit of the oil palm tree, ground-nut seed and soya bean seed are the most widely produced edible oils in the country today and are the common cooking ingredient in Africa, South East Asia and parts of Brazil and other parts of the world [16]. To the best of our knowledge no study has been conducted in our environment to evaluate the concentration of heavy metals present in edible oil and the potential hazards such contamination may pose to human health although studies on heavy metals have mostly been carried out on soil, water, paint and food [17]. This study thus aims at investigating the levels of the heavy metals Cd, Cr, Cu, Fe, Ni, Pb and Zn in edible oils sold in different markets in Benue and Taraba state, Nigeria.

2. Materials and Methods

The edible oil samples (palm oil, ground-nut oil and soya bean oil) were purchased from different markets in Benue (located in Otukpa, Makurdi, Katsina-Ala) and Taraba (located in Wukari, Ibi, Takum) states while the control edible oil (palm oil, ground-nut oil and soya bean oil) were bought from local producers in selected villages from each state where there is no industrial activity. A total of 90 edible oil samples (palm oil, ground-nut oil and soya bean oil) each were purchased for the two states studied. 15 composite samples were then analysed.

The method 3031 developed acid digestion of Oils for metal analysis by Atomic Absorption or ICP spectrometry was used in the preparation of the edible oil samples for the determination of total metal content in this study [18]. 0.5 g of the representative sample was mixed with 0.5 g of finely ground potassium permanganate and then 1.0 ml of concentrated sulphuric acid was added while stirring. A strong exothermic reaction was observed. The sample was then treated with 2 ml concentrated nitric acid. 10 ml of concentrated HCl was added and the sample heated until the reaction was complete. It was then filtered. The filter was washed with hot concentrated HCl. The filter paper was transferred to a digestion flask and treated with 5 ml of concentrated hydrochloric acid. To remove the manganese, the digestate was neutralized with concentrated ammonium hydroxide. Water and ammonium phosphate were added and the digestate stirred while a precipitate of manganese ammonium phosphate was formed. When the precipitation was complete, the digestate was filtered. The ammonia was then boiled off. The sample is brought to volume and analyzed on Flame atomic absorptiion spectrophotometer (FAAS). Standards were prepared with serial dilution techniques within the range of each metal determined. The standards used were Analar grade; the instrument was first calibrated with stock solutions of the prepared standards before being analyzed using Flame Atomic Absorption Spectrophotometer. After every five sample analyzed using FAAS, the first sample was repeated for quality check. Only when the result was within 10% of earlier readings did the analysis proceed further. The data obtained in the study were analyzed using Pearson correlation analysis.

3. Result and Discussion

The results of heavy metal concentrations in the edible oil (palm oil, ground-nut oil and soya bean oil) samples are presented in Tables 1, 2, 3 and summaries of the results are presented in Table 4. The edible oil samples bought from different markets in the two states revealed elevated levels of the heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The mean concentrations of heavy metals obtained in edible oils from the control area were much lower than those obtained from the edible oil (palm oil, ground-nut oil and soya bean oil) bought from the different market places under consideration. This reflects heavy metal contamination of edible oils (palm oil, ground-nut oil and soya bean oil) bought from these market places. For palm oil and ground-nut oil samples, out of the heavy metals considered, lead showed the highest level of contamination. The overall results (µg/g) in palm oil sample ranged from 0.028-0.076, 0.035-0.092, 1.011-1.955, 2.101-4.892, 0.666-0.922, 0.054-0.095, 0.031-0.068 and 1.987-2.971 for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively, while for the ground-nut oil sample the overall results ranged from 0.011-0.042, 0.011-0.052, 0.133-0.788, 1.789-2.511, 0.078-0.765, 0.045-0.092, 0.011-0.028 and 1.098-1.997µg/g for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively. For the soya bean oil samples, out of the heavy metals considered Cd and Ni showed the highest level of contamination, the overall results in soya bean oil samples ranged from 0.011-0.015, 0.017-0.032, 0.453-0.987, 1.789-2.511, 0.089-0.321, 0.011-0.016, 0.012-0.065 and 1.011-1.997µg/g for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively.

Generally, in the three edible oils (palm oil, ground-nut oil and soya bean oil) studied, the concentration of the heavy metals were high compared to the concentration of the heavy metals in the edible oils (palm oil, ground-nut oil and soya bean oil) obtained as control. This is an indication that these heavy metals are the primary contaminants in the edible oils (palm oil, ground-nut oil and soya bean oil) bought from these various markets place. This was reflected in the low level of these heavy metals obtained as control areas in comparison with those obtained from the market place. Also, the degree of heavy metal contamination of the edible oils (palm oil, ground-nut oil and soya bean oil) which were determined by its transfer factor was also high. From the mean results and transfer factor, there is a clear indication that the heavy metals determined (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) are the most contaminants of the edible oils (palm oil, ground-nut oil and soya bean oil) bought from these various markets place in Benue and Taraba state. All the samples (palm oil, ground-nut oil and soya bean oil) contained detectable amounts of these heavy metals of interest which were determined in the study. Lead, a ubiquitous and versatile metal was also detected in the edible oils examined. It has become widely distributed and mobilized in the environment and human exposure to and uptake of this non-essential element has consequently increased [11]. At high levels of human exposure, there is damage to almost all organs and systems, most importantly the central nervous system, kidneys and blood, culminating in death at excessive levels. At low levels, haem synthesis and other biochemical processes have been reported to be affected by lead contamination [18, 19, 20]. Lead continues to be a significant public health problem in developing countries where there are considerable variations in the sources and pathways of exposure, therefore there need for caution in the processing and handling of edible oils in order to reduce contamination of this metal from the environment. Chromium can irritate the skin and cause ulceration at low exposures while long term exposure can cause kidney and liver damage. It can also cause damage to circulatory and nerve tissues. Copper is the strongest pro-oxidant for oils and for the best stability, the content of copper should be below 0.02 ppm µg/g [21, 22]. The contamination of copper may be due to the degradation and deterioration of some metal alloys of iron equipment, being utilized for the treatment, storage and purification of the oils. High doses of copper can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from over exposure to copper. Long term exposure to cadmium is associated with renal dysfunction. Cadmium is bio persistent and once absorbed remains resident for many years. High exposure can lead to obstructive lung diseases and has been linked to lung cancer. Cadmium may also cause bone defects in humans and animals. The average daily intake for humans is estimated to be 0.15µg from air and 1µg from water [23]. Manganese is known to block calcium channels and with chronic exposure results in CNS dopamine depletion. This duplicates almost all of the symptomology of Parkinson's disease. Excessive amounts of nickel can be mildly toxic. Long term exposure can cause decreased body weight, heart and liver damage and skin irritation; the symptoms of exposure to some poisonous nickel compounds include nausea, vomiting, headaches and sleeplessness. The symptoms get worse later on from 12 to 24 hours after exposure and include palpitation, difficulty in breathing, chest pains and extreme fatigue. Nickel is rarely poisonous, but certain nickel compounds are extremely dangerous. The most common is nickel carbonyl in refineries, nickel mines and plating factories [24, 25, 26]. Correlations were established among the various metals under consideration as shown in Table 5. Generally the correlations among the metals were very poor, there was negative correlation between the pair of Pb /Zn in palm oil sample, in ground-nut oil there were positive correlation between the pair of Cd/Cu, Cd/Mn and negative correlation between pair of Cd/Ni while in soya bean oil there was positive correlation between the pair of Cd/Fe, this correlation between Cd and these metals may probably indicate that they emerged from the same origin or anthropogenic sources.

Factors influencing the toxicity of metals include interactions with essential metals, formation of metal-protein complexes, age and stage of development, lifestyle factors, chemical form or speciation and immune status of host [27]. It is known that significant percentage of Nigerian population consume edible oils both as nutritional and medicinal agents. It is good news that the edible oil samples analysed contained these toxic metals of interest at concentrations lower than the USP specification but if accumulated in the body over time may pose a risk to the health of consumers after many years.

4. Conclusion

The results obtained from the analysis of the edible oils (palm oil, ground-nut oil and soya bean oil) bought from various markets of Benue and Taraba state in Nigeria indicated that the concentrations of the heavy metals determined (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were higher than those found in the control samples. The degree of contamination of Pb was the highest. Cd, Cr, Cu, Fe, Mn, Ni and Zn also showed high degree of contamination in edible oils. From this reason, it could be predicted that the contaminations of these heavy metals determined; Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are probably from anthropogenic sources. The observed contaminants were Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn and their concentrations and factors of accumulations were high in all the edible oils studied. Edible oils have been part of human diet from the beginning of human life. For generations, it has been recognised as both a nutritious food and a valuable medicine. However, care should be taken to evaluate the purity and safety of this nutritional and medicinal agent to the human system. In as much as the edible oil samples (palm oil, ground-nut oil and soya bean oil) analysed contained these toxic metals of interest at concentrations lower than the USP specification if allowed to accumulate in the body over time it may pose risk to the health of consumers after many years. Hence, there is a need for closer monitoring of heavy metals in the other edible oils sold in the Nigeria markets and also enlightenment campaigns to consumers on likely ways to avoid contamination of edible oils such as the containers in which they are kept.

Table 1. *Heavy Metal Contents (μg/g) of Palm Oil sold in local market in Benue and Taraba State of Nigeria.*

Sites	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	0.076	0.057	1.112	3.511	0.922	0.095	0.041	2.123
2	0.063	0.059	1.955	2.521	0.831	0.065	0.031	2.971
3	0.042	0.049	1.856	2.975	0.701	0.075	0.032	2.554
4	0.035	0.035	1.788	2.245	0.744	0.067	0.044	2.065
5	0.045	0.056	1.678	2.331	0.875	0.061	0.043	2.876
6	0.065	0.088	1.835	2.859	0.666	0.087	0.065	1.997
7	0.075	0.045	1.699	2.222	0.698	0.092	0.055	2.543
8	0.054	0.075	1.589	2.789	0.844	0.077	0.052	2.234
9	0.048	0.067	1.023	2.208	0.689	0.054	0.032	2.543
10	0.053	0.073	1.011	2.156	0.801	0.071	0.041	2.675
11	0.063	0.092	1.955	3.999	0.788	0.055	0.033	2.654
12	0.028	0.088	1.654	2.115	0.732	0.085	0.055	2.098
13	0.067	0.075	1.896	2.101	0.841	0.065	0.061	2.012
14	0.057	0.077	1.105	4.892	0.887	0.081	0.041	2.122
15	0.033	0.054	1.786	3.401	0.771	0.075	0.068	1.987
Mean	0.054	0.066	1.596	2.822	0.786	0.074	0.046	2.364
S.D	0.015	0.017	0.350	0.818	0.079	0.013	0.012	0.339
MIN	0.028	0.035	1.011	2.101	0.666	0.054	0.031	1.987
MAX	0.076	0.092	1.955	4.892	0.922	0.095	0.068	2.971

Table 2. *Heavy Metal Contents (μg/g) of Ground nut Oil sold in local market in Benue and Taraba State of Nigeria.*

Sites	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	0.023	0.056	0.432	2.511	0.122	0.045	0.012	1.231
2	0.012	0.042	0.231	2.321	0.131	0.065	0.017	1.971
3	0.042	0.022	0.653	1.975	0.765	0.055	0.012	1.554
4	0.035	0.011	0.788	2.245	0.144	0.067	0.011	1.767
5	0.025	0.012	0.678	2.331	0.175	0.061	0.013	1.876
6	0.011	0.028	0.133	1.859	0.166	0.087	0.018	1.997
7	0.013	0.017	0.699	2.222	0.098	0.092	0.021	1.543
8	0.015	0.021	0.589	1.789	0.144	0.077	0.016	1.234
9	0.017	0.025	0.321	2.208	0.089	0.054	0.011	1.543
10	0.021	0.029	0.431	2.156	0.201	0.071	0.019	1.675
11	0.023	0.026	0.444	1.999	0.078	0.055	0.014	1.654
12	0.028	0.019	0.333	2.115	0.132	0.045	0.012	1.098
13	0.012	0.018	0.237	2.101	0.141	0.065	0.013	1.123
14	0.019	0.029	0.387	1.892	0.211	0.081	0.011	1.543
15	0.023	0.023	0.298	2.401	0.171	0.055	0.028	1.987
Mean	0.021	0.025	0.444	2.142	0.185	0.065	0.015	1.586
S.D	0.009	0.011	0.196	0.209	0.165013	0.014	0.005	0.307
MIN	0.011	0.011	0.133	1.789	0.078	0.045	0.011	1.098
MAX	0.042	0.056	0.788	2.511	0.765	0.092	0.028	1.997

Table 3. *Heavy Metal Contents (µg/g) of Soybean Oil sold in local market in Benue and Taraba State of Nigeria.*

sites	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	0.013	0.019	0.987	2.511	0.122	0.016	0.021	1.123
2	0.015	0.026	0.897	2.321	0.131	0.013	0.031	1.971
3	0.012	0.017	0.856	1.975	0.201	0.012	0.012	1.554
4	0.014	0.018	0.788	2.245	0.144	0.011	0.044	1.011
5	0.012	0.022	0.678	2.331	0.175	0.012	0.043	1.876
6	0.011	0.021	0.835	1.859	0.166	0.014	0.065	1.997
7	0.012	0.032	0.699	2.222	0.098	0.011	0.055	1.543
8	0.011	0.021	0.589	1.789	0.144	0.015	0.022	1.234
9	0.013	0.023	0.543	2.208	0.089	0.012	0.032	1.543
10	0.015	0.018	0.453	2.156	0.201	0.011	0.041	1.675
11	0.012	0.025	0.555	1.999	0.321	0.012	0.033	1.654
12	0.014	0.023	0.567	2.115	0.132	0.014	0.025	1.098
13	0.011	0.024	0.896	2.101	0.141	0.016	0.061	1.133
14	0.012	0.019	0.762	1.892	0.122	0.012	0.041	1.098
15	0.015	0.023	0.786	2.401	0.171	0.015	0.028	1.987
Mean	0.013	0.022	0.726	2.142	0.157	0.013	0.037	1.499
S.D	0.001	0.004	0.158	0.209	0.0559	0.002	0.015	0.360
MIN	0.011	0.017	0.453	1.789	0.089	0.011	0.012	1.011
MAX	0.015	0.032	0.987	2.511	0.321	0.016	0.065	1.997

Table 4. *Summaries of results of Heavy Metal contents (µg/g) of some edible oils sold in some selected local markets in Benue and Taraba state of Nigeria.*

Metals	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Palm Oil								
Mean	0.054	0.066	1.596	2.822	0.786	0.074	0.046	2.364
S.D	0.015	0.017	0.350	0.818	0.080	0.013	0.013	0.339
Range	0.028-0.076	0.035-0.092	1.011-1.955	2.101-4.892	0.666-0.922	0.054-0.095	0.031-0.068	1.987-2.971
Control	0.005	0.004	0.100	0.150	0.052	0.005	0.002	0.251
T.F	10.800	16.500	16.000	18.813	15.115	14.230	23.000	9.418
Ground-nut Oil								
Mean	0.021	0.025	0.444	2.142	0.185	0.065	0.015	1.586
S.D	0.009	0.011	0.196	0.209	0.165	0.014	0.005	0.307
Range	0.011-0.042	0.011-0.052	0.133-0.788	1.789-2.511	0.078-0.765	0.045-0.092	0.011-0.028	1.098-1.997
Control	0.003	0.002	0.050	0.189	0.024	0.006	0.001	0.240
T.F	7.000	12.500	8.880	11.333	7.708	10.833	15.000	6.608
Soya bean Oil								
Mean	0.013	0.022	0.726	2.142	0.157	0.013	0.037	1.500
S.D	0.001	0.004	0.158	0.209	0.056	0.002	0.015	0.360
Range	0.011-0.015	0.017-0.032	0.453-0.987	1.789-2.511	0.089-0.321	0.011-0.016	0.012-0.065	1.011-1.997
Control	0.001	0.002	0.095	0.185	0.035	0.001	0.003	0.340
T.F	13.000	11.000	7.642	11.578	4.486	13.000	12.333	4.412

Table 5. *Inter-elemental correlation of heavy metals in edible oils (palm oil, ground-nut oil and soya-bean oil).*

Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	0.133	-0.081	0.186	0.274	0.258	-0.060	0.133
		-0.064	0.248	0.037	-0.056	0.132	-0.141
			-0.151	-0.261	-0.152	0.266	0.027
				0.377	0.158	-0.151	-0.198
					-0.004	-0.167	0.056
						0.449	-0.475
							-0.686
	-0.235	0.560	0.107	0.644	-0.513	-0.323	-0.022
		-0.441	0.294	-0.090	-0.237	-0.008	-0.042
			0.067	0.268	0.094	-0.198	-0.054
				-0.250	-0.471	0.194	0.174
					-0.120	-0.143	0.029
						0.285	0.254
							0.463
	-0.072	-0.118	0.609	-0.056	-0.183	-0.320	0.191
		-0.083	0.172	-0.146	-0.031	0.329	0.269
			0.282	-0.258	0.455	0.072	-0.044
				-0.239	0.075	-0.131	0.141
					-0.166	-0.124	0.314
						-0.110	-0.152
							0.121

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