Elemental Content of Wines Marketed on Ghanaian Markets

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Abstract
The concentrations of four metals (Cu, Zn, Fe and Sn) were determined in nine wine brands by flame atomic absorption spectrometer (FAAS) after digesting the wine samples with HNO_3-H_2O_2 mixture. Among the metals analyzed iron was found to have the highest concentration (0.2-5.6, average: 1.629 mg/L) followed by copper (0.03-0.14, average: 0.108 mg/L), tin (0-1.82, average: 0.166 mg/L) with Zn being the least (0-0.22, average 0.02 mg/L). The established contents of Cu and Zn showed that wines sold on Ghanaian market could serve as good dietary sources of the essential trace metals, and the determined values were within the allowed metal levels in wines for human consumption. The highest consumption of Fe, Cu, Zn and Sn based on daily intake of trace metals were from the consumption of red wines for both adults and children.
Keywords: wine, flame atomic absorption spectrometer

1.0 Introduction
Chemicals in a number of foods contain toxic substances and may not pose a hazard if consumed in allowable amounts. A number of minerals can produce chronic toxicity when absorbed and retained in excess of the body's demands. The toxicity of these metals is a function of their physical and chemical properties as well as the dose that enters the body. Toxicity is also a function of the ability of metals to bioaccumulate in body tissues and for this reason, it is very important to have adequate information about the chemical forms of metals.

Wine is among the beverages which contribute to increasing the total dietary intake of trace elements to an extent greater than 10 % (Minoia *et al.,* 1994). Numerous studies have shown that a moderate consumption of wine, especially red, improves good health and longevity when it is combined with a balanced diet (Klatsky et al., 1992). Grapes accumulate small amounts of toxic metals by translocation from the roots or by direct contact with vineyard sprays. Although its elemental content can be a source of essential minerals and trace elements to human beings, there is also a universal concern for the heavy metals and other trace elements present in musts and wines.

The elemental content of wines depends upon factors such as the type of ground and underground soil of the vineyard, the climatic conditions of the geographical region (temperature, sun exposure, proximity to sea, and amount of rainfall), the proximity of the vineyard to areas of high traffic and to areas overburdened with industrial activities, the agrochemical treatment of the vine plant, the vinification methods, the wine-processing equipment and, finally, the type of storage container, including the type of the cork used for bottling (Núñez *et al*., 2000).

Daily consumption of wine in reasonable quantities contributes significantly to the requirements of the human organism for essential elements. On the other hand, numerous metals, such as Pb, Cd and As, are known to be potentially toxic. At the same time, the analysis for certain elements in wines is of special concern due to their toxicity in case of excessive intake, and also the effect they seem to have on the organoleptic properties of wine (Galani-Nikolakaki et al.; 2002).

2.0 Materials and Method
2.1 Sample treatment
All determinations were carried out on untreated wine samples; only nitric acid was added to lower pH (1 ml concentrated acid to 100ml sample, the resulting pH being ~1.5).

2.2 Sampling
The study was carried out with three batches of samples from selected markets in the Accra Metropolitan Assembly. A total of nine (9) wine samples; seven (7) red and two (2) white wines samples were collected. Samples were taken in triplicates from each bottle. Each metal was estimated 3 times in each sample of wine.

2.3. Apparatus
All glassware was soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid. It was rinsed with double distilled water and dried before using.

2.4 Reagents
All the reagents and chemicals used were of analytical grade Merck (Darmstadt, Germany) but concentrated 65% HNO_3 and 30% H_2O_2 were of spectroscopic grades. Standard solutions of heavy metals (1000 mg/l) namely, copper (Cu), Iron (Fe), tin (Sn) and Zinc (Zn).

2.5 Determination of metals in wine samples by FAAS
Fe, Cu, Zn, and Sn were determined by AAS using an air/acetylene flame. Elements were analyzed by further diluting the digested wine samples. Dilution was required to bring the concentration within the linear range of the calibration. All the analyses were carried out using flame atomic absorption spectrophotometer at the wavelengths specific for each metal.

2.6 Daily intake of Metals
The daily intake of metals (DIM) was calculated by the following equation:

$$DIM = \frac{(M) \times K \times I}{W}$$

Where (M), K, I and W represent the heavy metal concentrations in wine (mg/l), conversion factor, daily intake of vegetables and average body weight, respectively. The conversion factor used to convert wine weight to dry weight was 0.085, as described by Rattan, Datta, Chhonkar, Suribabu, and Singh, 2005. The average adult and child body weights were considered to be 55.9 and 32.7 kg, respectively, while average daily wine intakes for adults and children were considered to be 0.345 and 0.232 kg/person/day, respectively, as reported in the literature (Ge, 1992; Wng, Sato, Xing, and Tao, 2005).

2.7 Statistical analysis
Mean values obtained for the metals studied in the nine brands of wine samples were compared by One-Way ANOVA at 95% level using SPSS 16 for windows (SPSS Inc.) assuming that there were significant differences among them when the statistical comparison gives $p < 0.05$.

3.0 Results and Discussion
The source of elemental species in foodstuffs can be either anthropogenic or natural. In the first case it is a result of external contamination (environmental; occurring during processing or leaching from packaging materials). Naturally it may result from an endogenous synthesis by a plant or an animal (methylmercury, organoarsenic, or organoselenium species).

Four trace metals Fe, Cu, Sn and Zn were detected in the wine samples analyzed. Iron (Fe) and Copper (Cu) were identified in all wine samples analyzed. Zinc (Zn) and Tin (Sn) were found in 9.1% of the samples analyzed. From table 1.0, iron had the highest concentration in all samples (0.2-5.6, average: 1.629 mg/L) analyzed followed by copper (0.03-0.14, average: 0.108 mg/L), tin (0-1.82, average: 0.166 mg/L) with Zn being the least (0-0.22, average 0.02 mg/L). Our study indicated significant differences in iron content between different wine brands analyzed.

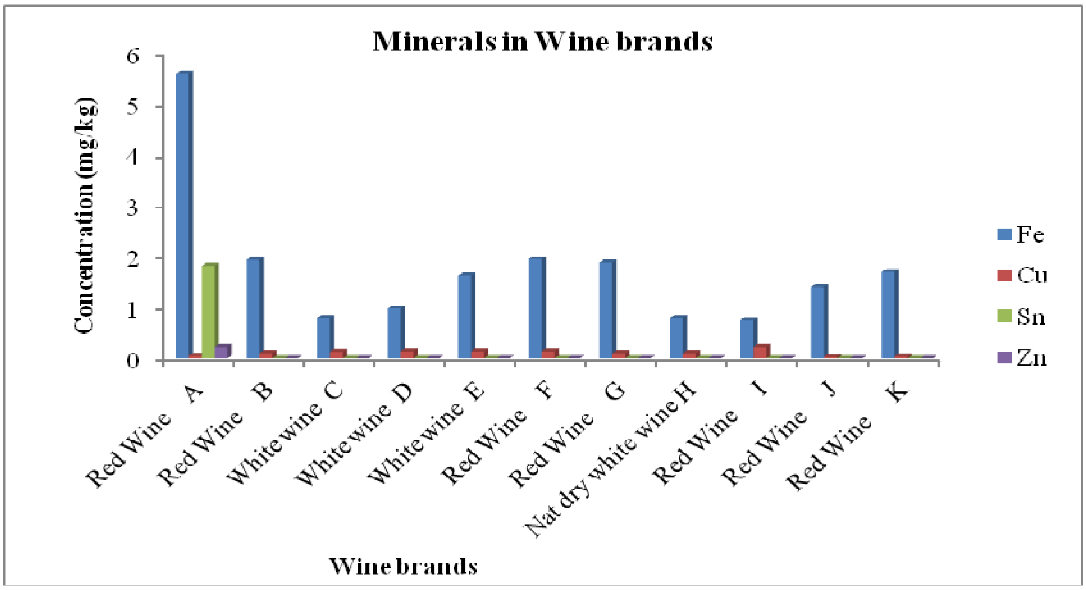

Fig. 1.0 Trace metals in different wine brands on Ghanaian markets

Table 1.0

Daily intake of metals (mg) for individual heavy metals in different wine brands

Results	Fe		Cu		Zn		Sn	
	Adults	children	Adults	children	Adults	children	Adults	children
RW A	0.00294	0.00338	0.00003	0.00003	0.00012	0.00013	0.00096	0.00110
RWB	0.00100	0.00120	0.00005	0.00006	0.00000	0.00000	0.00000	0.00000
WC	0.00042	0.00048	0.00007	0.00008	0.00000	0.00000	0.00000	0.00000
WD	0.00051	0.00059	0.00007	0.00008	0.00000	0.00000	0.00000	0.00000
WE	0.00086	0.00098	0.00007	0.00008	0.00000	0.00000	0.00000	0.00000
RWF	0.00001	0.00120	0.00007	0.00008	0.00000	0.00000	0.00000	0.00000
RWG	0.00099	0.00113	0.00005	0.00006	0.00000	0.00000	0.00000	0.00000
RWH	0.00042	0.00048	0.00005	0.00006	0.00000	0.00000	0.00000	0.00000
RWI	0.00039	0.00045	0.00012	0.00013	0.00000	0.00000	0.00000	0.00000
RWJ	0.00073	0.00084	0.00002	0.00002	0.00000	0.00000	0.00000	0.00000
RWK	0.00011	0.00012	0.00002	0.00002	0.00000	0.00000	0.00000	0.00000

Table 1 shows that maximum Fe accumulation was in RWA, whereas RWI contained the maximum concentration of Cu. Red wines showed a higher concentration of Cu compared to the white wines.

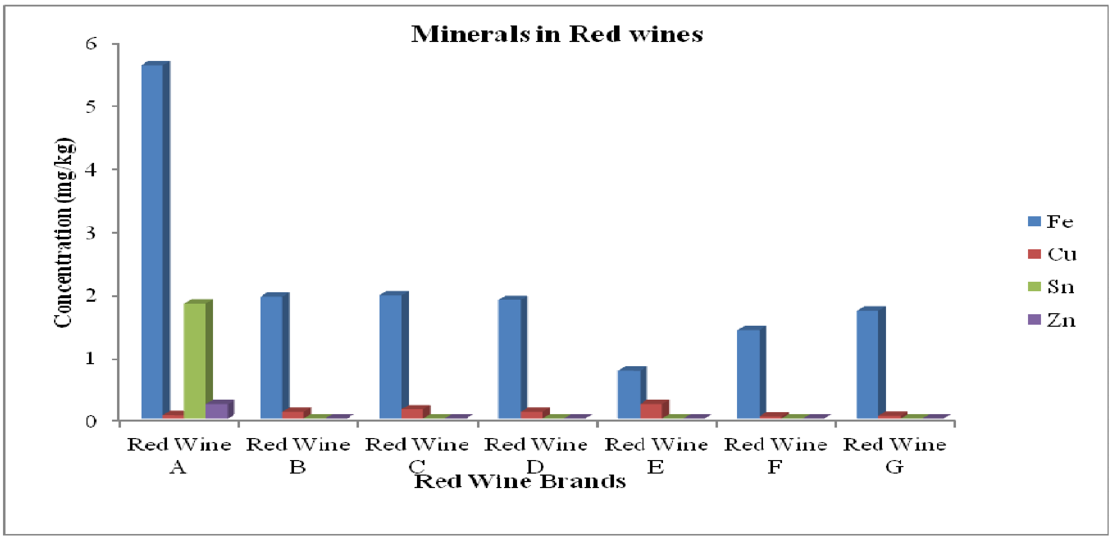

Fig 2.0 Trace metals in red wine brands on Ghanaian markets

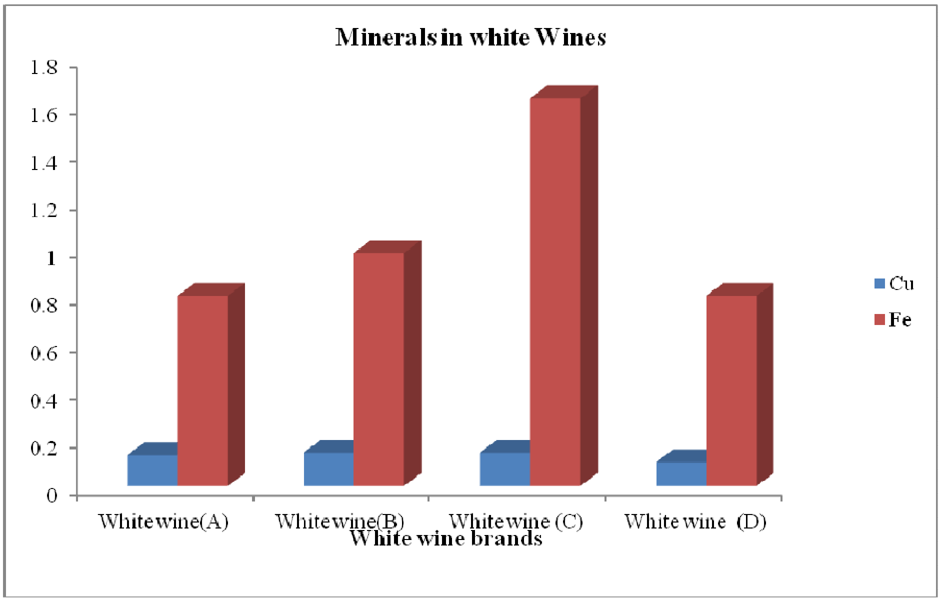

Fig 3.0 trace metals in white wines in Ghanaian markets

In view of its acidity, wine is likely to corrode metal winemaking equipment, thus dissolving some toxic cations and others responsible for metallic casse. This property may also be utilized when wine is racked, by using copper equipment to eliminate certain thiols and especially hydrogen sulphide, in the form of copper salts, which are particularly insoluble.

3.1 Iron (Fe)

Iron was found in substantial quantities in all wine varieties. The red wines recorded higher concentrations of iron compared to the white wines. The (Fe^{3+}) / (Fe^{2+}) ratio in wine depends on storage conditions, especially the free sulphur dioxide concentration. According to Marengo and Aceto (2003) the iron content of wines may be partly due to natural sources and partly to technological processes. Natural sources include the soil, the percentage of iron in the dust covering the grapes prior to vintage, and the atmospheric pollution during the same period. A natural source of iron in the grapes is mitochondria, which are composed of iron–porphyrin–protein complexes, and they degrade during wine fermentation, releasing iron into the wine (Hsia *et al.,* 1975). The differences in Fe concentrations in different wine brands may be attributed to geographical location, atmospheric deposition of airborne particulate matter on grapes, transfer of metals from the soil via the roots to the grapes, maturity and variety of grapes, and climatic conditions during growth of grapes. The observed variability in the

Fe content of analyzed wines may also be ascribed to culture and wine making practices, capacity of grapes to take up mineral substances, yeasts, processing equipment, conservation and bottling (Lazos and Alexakis,1998).

3.2 Copper (Cu)

Low levels of copper were identified in all the samples analyzed .There were no significant differences in the concentrations of copper in red and white wine samples. Copper concentrations found in analyzed samples may originate partially from enzymes, especially oxidases, which are found in abundance on fresh grapes (Hsia *et al.,* 1975). In musts and fresh wines, copper concentration is usually 0.1–0.3 mg/L. Amerine and Ough (1980) reported that for concentrations greater than 0.5 mg/L there is the possibility of haze formation. According to Eschnauer and Stoeppler (1992) the main sources of copper in wines include the winery equipment made of copper alloys, fungicides and the addition of copper sulfate salts during the stage of vinification.

Copper concentrations may increase during aging due to contact with equipment made of copper, tin or bronze. The prolonged aging of wine on its yeast lees causes a significant decrease in oxidation– reduction potential, which favours the reduction of copper and, consequently, the appearance of copper casse. At the same time, the presence of yeast lees promotes the fixing of copper (Eschnauer and Stoeppler, 1992).

3.3 Zinc

Zn was identified in one out of the seven red wine samples analyzed. Zn is essential as a constituent of many enzymes involved in a number of physiological functions, such as protein synthesis and energy metabolism. Zn deficiency resulting from poor diet, alcoholism and malabsorption, causes dwarfism, hypogonadism. Traces of zinc are naturally present in must and wine. Higher concentrations of this trace metal may come from the vineyard, due to galvanized iron wire damaged by mechanical harvesting, or dithiocarbamate-based fungicides. Another source is winemaking equipment made of alloys, such as bronze pumps, hose connections, taps. Prolonged maceration of grape solids leads to an increase in zinc concentrations.

3.4 Tin (Sn)

Tin was detected in one of the red wine samples analyzed. Tin is seldom found in wines, and its presence, when detected, may be due attributed to contact of wines with tin utensils or tin-plated equipment or containers. Tin can also react with sulphites present in wine, resulting in the formation of hydrogen sulphide and free sulphur (Amerine *et al.,* 1972).

Table 2.0 ANOVA TABLE

		Sum of Squares	df	Mean Square	F	Sig.
Wine concentration	Between Groups	19.461	3	6.487	10.915	.000
	Linearity	1.136	1	1.136	1.912	.174
	Deviation from Linearity	18.325	2	9.162	15.416	.000
Trace metals	Within Groups	23.774	40	.594		
	Total	43.235	43			

Table 2.1 Test of homogeneity of variance

Levene Statistic	df 1	df 2	Sig.
4.879	3	40	0.006

The homogeneity of variance assumption was met as the results suggested that 0.6 times out of 100 variances accounted for differences observed within the four minerals (Cu, Fe, Zn and Sn) would be obtained due to chance.

The absence of other trace elements in the eleven wine samples analyzed may be due to the absorption of the metals onto yeast cells which are removed from the final product during the prefermentation clarification (a process of removal of substances that produce unwanted flavours, favour the fermentation to dryness and increase the fermentation rate. This is corroborated by Garrido *et al.,* 1997.

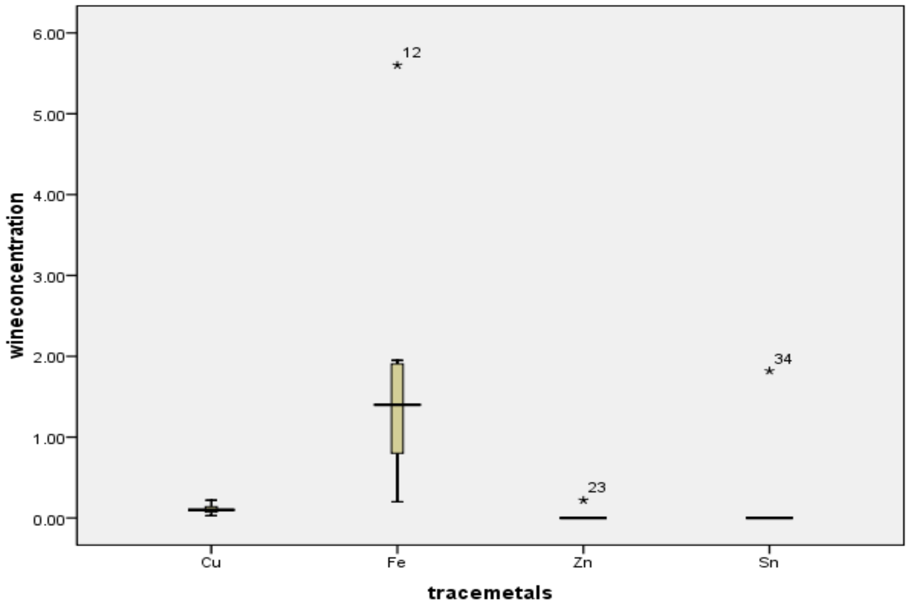

Fig 4.0 Box plot of trace elements in wine.

From the box plot, Cu and Fe had their median approximately in the middle of their boxes but large overlap between the boxes. This suggests that there were significant differences in wine concentrations with respect to Fe and Cu and that there was one statistical outlier with respect to Fe in wine samples analyzed. The uneven whiskers of the boxes also suggest significant differences in Cu and Fe wine concentrations.

3.5 Daily Intake of Trace Metals (DIM)
To assess the health threat of any contaminant, it is imperative to estimate the level of exposure, by detecting the routes of exposure to the target organism. Food is the main source of human exposure to contaminants. The DIM values for heavy metals were high when based on the consumption of red wines. The highest consumption of Fe, Cu, Zn and Sn were from the consumption of red wines for both adults and children. The findings regarding DIM of this study suggest that the consumption of red wines is high compared with white wines as dietary intake of limits of Cu, Fe and Zn in adults can range from 1.2 to 3.0 mg, 10.0 to 50.0 mg, and 5.0 to 22.0 mg respectively (WHO, 1996).

4.0 Conclusion
It is essential to ascertain the elemental content of wines should be determined because excess is detrimental due to potential toxicity and risks to human health, consequently imposing the maximal allowed values and/or prohibited limits. The contents of the investigated metals (Fe, Sn, Cu and Zn) in wine samples from Ghana are considerably lower than the maximum concentrations allowed.

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