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Original Research Article

Elemental composition of vegetables in the Dar es Salaam market using wavelength dispersive x-ray fluorescence analysis

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Abstract

Concentrations of several elements were determined in vegetables collected from the Dar es Salaam City markets by Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF). The method involved taking 1g of dried and finely grinded vegetables prepared as pellets for analysis. Vegetables analyzed belong to species of Vigina Unguiculata (Kunde), Amarathus (African Spinach), Cucuta maxima (Pumpkin), and Brassica Chinese (Spinach). The WDXRF SRS 300 with Rh anode was operated at 60kV, 5mA and 60kV, 50mA for different range of elemental analysis. In all the vegetable samples carbon and oxygen were found to dominate with high concentrations between 32% and 47%. This paper presents results for elemental concentrations in vegetables that are main meal of any average Dar es Salaam city resident.

Keywords: Wavelength Dispersive X-ray Fluorescence, Vegetables, vigina Unguiculata, Amarathus , Cucuta maxima, Brassica Chinese

INTRODUCTION

Trace analysis of biological materials plays an important role in enriching knowledge of what human beings feed on. It also determines the level of elemental concentration that can be excessive to human health. There have been a number of traces analyses of biological materials published but not much analysis have been performed on food materials in Tanzania. Recently WDXRF analysis has shown to be a very valuable technique both in terms of its detection limit and its accuracy, high sensitivity and its dynamism to thick samples.

There are various ways of calibrating the XRF spectrometer when it involves sample thicknesses of different particles sizes for which absorption of matrix and particle size effects have to be considered. Though the WDXRF spectrometer is applicable for different type of samples, calibration in WDXRF has commonly been attained using known standard materials or internal standards which have known concentrations. In 1990 TXRF (Total Reflection x-ray Fluorescence) (Koleleni and Van Grieken, 1990) was applied to measure vegetables material with detection limit from 1.4 ng to 12.57 ng (Aiginger and Wobrauschek, 1975) for most of the elements. The elements were digested and deposited (Aiginger and Wobrauschek, 1985) as a spot size on quartz plates for analysis. The advantages of TXRF (Muia et al.,1990) in comparison to WDXRF are the ability to measure a number of elements simultaneously and to deliver the quantitative information about the sample concentrations of the major elements within a very short time. On the other hand the drawbacks is that it has limited count rate, relatively low energy resolution and poor sensitivity to low atomic number elements and this is where WDXRF takes over (Parns et al., 2001). The cost of a TXRF instrument is lower than that of WDXRF and the smaller size and weight of the instrument allows for a portable system. XRF analysis has the following advantages (de Vito et al., 2001): low radiation damage, that is, the dominant interaction between a photon and the sample in the photoelectric effect is low, high accuracy especially when reference sample has similar chemical composition and

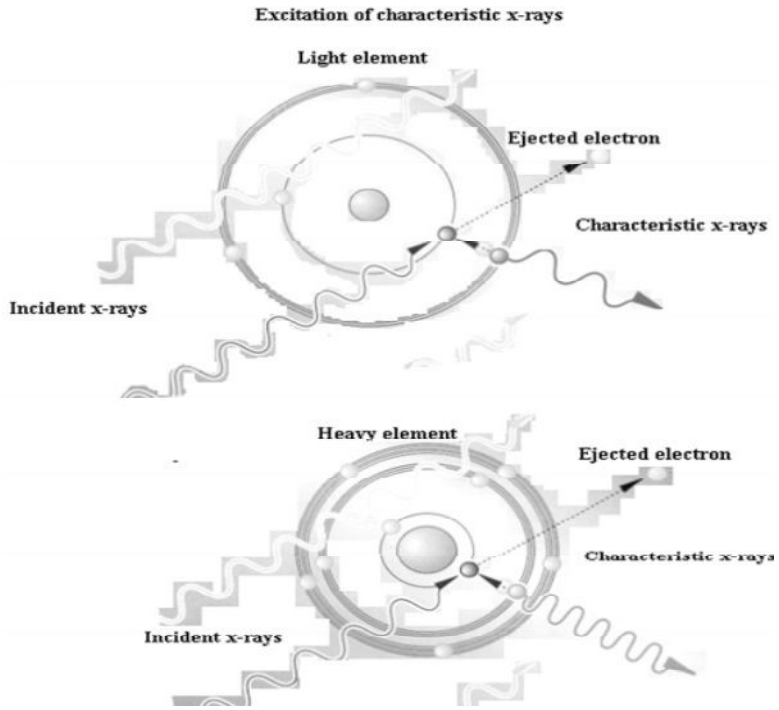


Figure 1. The excitation and de-excitation mechanism in the electronic shell of the atom

similar crystal or mineralogical structure as the sample and that the sample environment in XRF analysis can be performed in air or under ambient conditions with little or no sample preparation.

The WDXRF method has been applied for determination of major and trace analysis of biological material from Dar es salaam, Tanzania, collected between September 2003 and February 2004. The sample materials were obtained from food sold in the Dar es Salaam City markets. The concentration of trace and major elements serve as an indicator of both the toxicity and the nutrition value of the foodstuff involved. In this work we report the results of the analysis carried out as indicated above and the values obtained are compared to similar determinations elsewhere (Valkovic 1980, Pendias 1984).

Theory

Photons when incident on atom are absorbed by the shell electron. If it exceeds the binding energy of the shell it jumps to another shell. The vacancy left is filled by the electron for stability of the atom, thus characteristic X-rays are emitted in the processes. For the case of light element K lines are used as reference due to electronic transition while for heavy elements L lines are used. A very high energy excitation is needed to excite K lines of high Z elements and therefore L lines are used instead. The excitation and de-excitation mechanisms are illustrated in Figure 1.

Details on configuration, excitation and detection methods are articulately given by Helsen and Kuczmow in the Hand Book of X-ray Spectrometry (Van Grieken and Markowicz 2002).

Sample collection

Samples of the vegetables (Vigina Unguiculata (kunde), Amarathus (African Spinach), Cucuta maxima (Pumpkin), and Brassica Chinese (Spinach and mboga)) were collected from markets at different locations in Dar es salaam City namely Tabata, Kawe, Survey, Tegeta, Manzese, Kisutu, Kipawa, Kimara and Mwananyamala.

Preparation procedure

The samples were dried in the oven at a temperature of 50 ^{o}C. Each sample was then grinded using mortar and pestle then made into pellets. Samples of 7 g of dried powdered vegetables were mixed with 7 g of boric acid and pressed to form a pellet in disc form then kept in a container with silica jelly to absorb moisture ready for x-ray analysis. Under circumstances where pellets were not possible to make, fused discs were made instead.

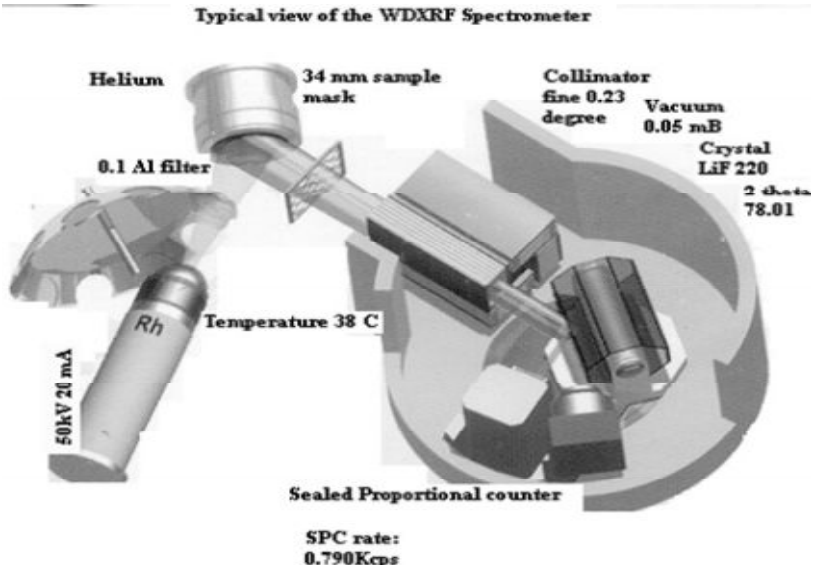


Figure 2. The Wavelength Dispersive X-ray fluorescence spectrometer in Dar es Salaam (SEAMIC).

Table 1. The Experimental conditions used for WD-XRF analysis.

Parameter	Rh
line	$K\alpha_1$
kV	60
mA	50
Filter	1mm Al
Collimator	fine
Crystal analyzer	LiF200
Order	1
2θ	80^0
+ offset	0.8^0
- offset	0.8^0
Detector	Prop. Counter/NaI (Tl)
Lower level	15
Upper level	90

Experiments

The pellet samples were placed on holders in a six position sample changer and excitation was conducted by SRS300, the sample analyzer machine equipped with Rh anode tube with spot focus operating under vacuum condition. The operating voltages vary from 20 kV to 60 kV with current from 50 mA to 5 mA. The characteristic x-ray from the sample were collimated before arriving at the analyzing crystal under a vacuum of 0.05 mB and detected using a proportional counter and NaI (Tl) x-ray detector biased at -1000V.The detector was connected to a pulse processor and other associated electronics. The net peak areas of the characteristic lines were determined using a non-linear least square fitting procedure. The whole detection and crystal system was shielded by a 10 mm lead shield. Analysis time ranged between 20-50 seconds for each element and about 100s for the standard sample. The spectrometry and its arrangement are shown in Figure 2 and Figure 3 respectively. Table 1 show the experimental conditions used in WDXRF analysis.

RESULTS AND DISCUSSION

The results obtained in the table 2 for S, Cl, K and Ti are very close to each other for African spinach (MCH), sweet potatoes (SWTP), and cassava (MHO) leaves which are biological materials taken as part of meal in Dar-es- salaam. The S content in the studied material is higher relative to other elements ranging from 0.168% to

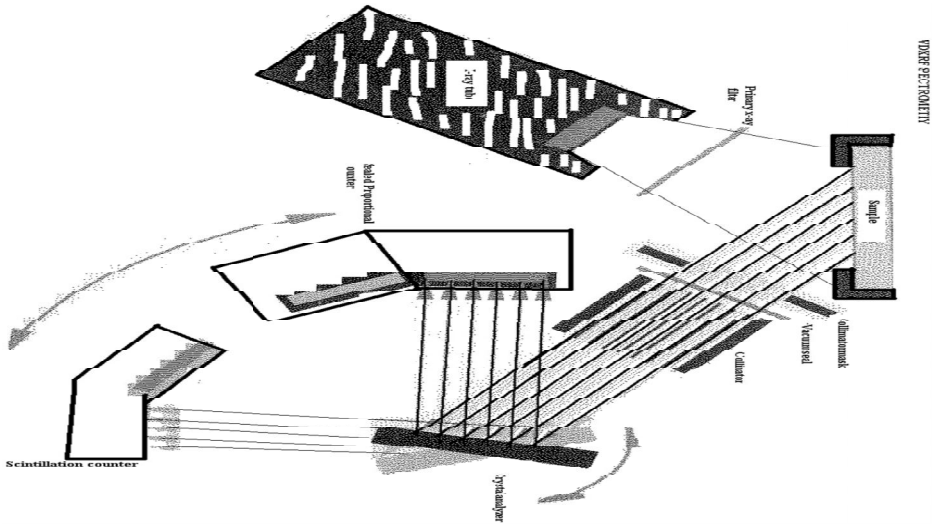


Figure 3. Schematic representation of the experimental arrangement for WDXRF.

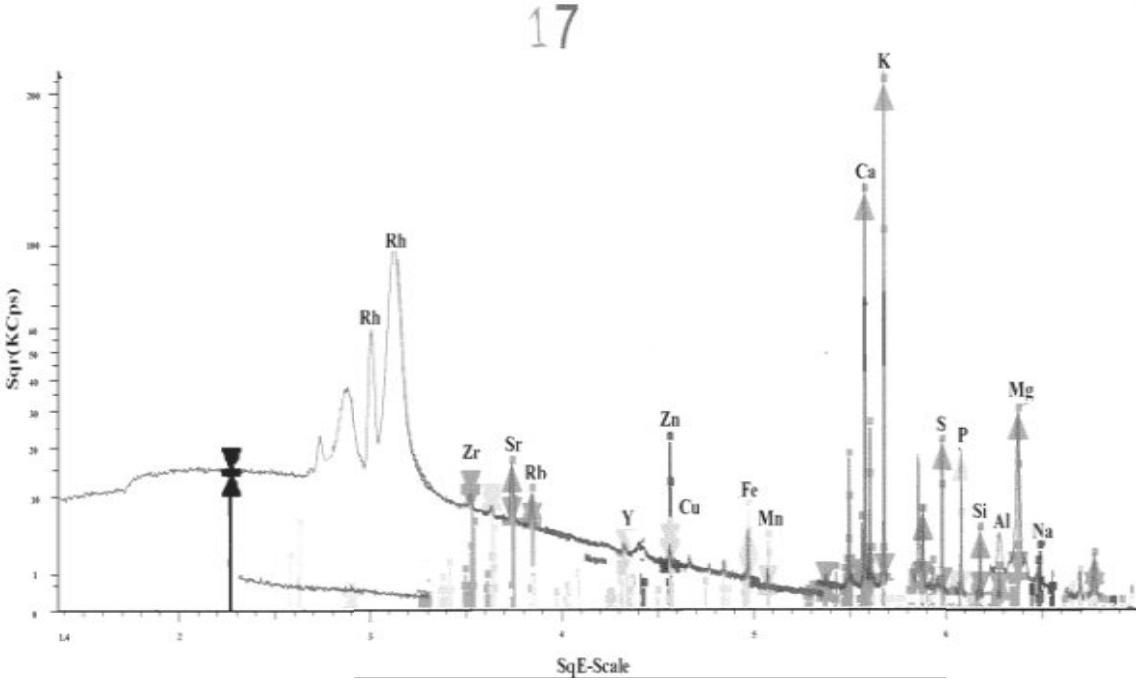


Figure 4. Typical spectrum for vegetable by WDXRF

0.244% while Cl values are varying. The values of Mn, Fe and Zn in these edible vegetables vary from one another with MHO having the significantly higher than 92 from MCH with value in MN and Zn of 105pmm, Br is observed in MCH and SWTP but does not appear in MHO and pumpkin (MBG) leaves. Similarly a low level of Rb of 20.01pmm and 15.9ppm appear in SWTP and MBG respectively but are not available in MCH and MHO. Sr has been found in all the vegetable material analyzed. Papaw (PPI) leaves are not eaten but bears a fruit consumed daily by people. The results obtained from PPI do not differ much from those the consumable ones (MCH, SWTP, MHO and MBG). The spectral variations for these samples are shown in figures 1-5 for MCH, MHO, MBG, SWTP and PPI respectively.

Table 3 shows the result for concentration ranges of five samples collected for each vegetable in 1993 and are compared with African spinach measured in this experiment currently. The results for MHO for all the

Table 2. Average results of biological samples

ELEMENT	MCH*	SWTP*	MHO*	PPI*	MBOGA
S	0.24%	0.18%	0.17%	0.147%	0.105
Cl	3.10%	2.20%	2.00%	0.23%	0.881
K	1.37%	1.05%	0.69%	0.25%	6.69
Ca	1.405%	1.09%	1.23%	1.52%	5.46
Ti	0.009%	-	-	-	0.0114
Mn	92ppm	38.238ppm	105ppm	52.755ppm	0.0152
Fe	958ppm	105ppm	107ppm	116.6ppm	0.0819
Zn	30.717ppm	15.210ppm	119.6ppm	23.825ppm	0.0122
Br	247ppm	147ppm	-	75ppm	-
Rb	-	20.008ppm	-	-	-
Sr	141.8ppm	56.99ppm	90.8ppm	94.426ppm	0.0268
Pb	-	-	-	-	-

*MCH- African Spinach, SWTP- Sweet potatoes, MHO- cassava, MBG- pumpkin, PPI- papaw, DL- Detection limit, Errors in the results are less than 5%.

Table 3. Results of the concentration ranges in from the biological samples.

Element	MCH*	SWTP*	MHO*	MBG*	PPI*	MCH
Cl	2.95-3.37%	2.23-2.93%	2.27-2.37%	1.24-1.65%	2.58-2.67%	0.24-0.53
K	1.20-1.60%	0.57-1.31%	0.65-0.75%	0.43-0.74%	0.27-440ppm	4.07-7.9
Ca	1.16-.160%	0.70-1.68%	1.18-1.29%	0.43-0.51ppm	1.29-1.53ppm	3.96-5.72
Ti	0.01-0.02%	5.91-49.82ppm	47.31-48.19ppm	22.92-410ppm	32.96-86.63ppm	0.01-0.014
Mn	0.01-0.11%	39.16-65.96ppm	110-120ppm	9.40-13.35ppm	56.90-69.58ppm	0.01-0.02
Fe	0.10-0.11%	0.01-0.02ppm	170-180ppm	0.01-0.02%	160-210ppm	0.03-0.07
Zn	0.01-0.01%	30.65-41.37ppm	140ppm	33.92-47.81ppm	40.70-47.81ppm	0.005-0.007
Br	0.02-0.03%	91.76-250ppm	29.17-48.18ppm	25.43-50.21ppm	210-240ppm	0.001-0.002
Rb	6.63-9.83ppm	3.50-35.30ppm	0-7.08ppm	20.96-23.15ppm	-	0.005-0.008
Sr	6.63-9.83ppm	41.00-110ppm	98.06-100ppm	61.21-62.35ppm	96.222-110ppm	0.013-0.023

- errors in the results are less than 5%

elements analyzed are very consistent throughout. The leaves for MHO were all matured when collected which might have been a contributing factor.

Volkovic (1980) published results for essential elements in plants (see table 4) whose range agrees at least approximately with the range of the results obtained for our biological materials measured in the experiment. Pendias and Pendias (1984) have given results (table 3) whose elemental concentrations are relatively large and might be toxic. The results for the analyzed materials as shown in table 3 indicate that the biological materials involved do not contain toxic elements and have reasonable elemental concentrations to be used as edible material to people. From Figure 5 the results show that some plants have their concentrations dominated by Nitrogen, Carbon and Oxygen. Amaranthus Species collected from Tabata, Tegeta and kimara was observed to contain Nitrogen of values 8.29%, 8.94% and 9.939% respectively while those from Kawe, Chuo Kikuu, Manzese, Temeke, Kisutu, Kipawa and Mwanyamala did not have Nitrogen. The Carbon and Oxygen elements were found at high concentrations in the sample because of carbohydrates contents. Otherwise some of the unexpected elements are a result of polluted irrigation water, deposition as a result of air pollution and the variations from different soil and fertilizer contents (especially N). From figure 6 the variation pattern of Si, P, S, Cl, K, Ca, Ti, Mn and Fe have similar pattern for all the

Table 4. Approximate concentration of trace elements in a matured leaf tissue generalized for various species compared to experimental results of those from Tanzania.

Element	Normal (pendias and pendias) in ppm	Excessive (pendias and pendias) in ppm	Essential (Valkovic) in ppm
S	-	-	100
Cl	-	-	100
K	-	-	10000
Ca	-	-	500
As	1.0-1.7	5-20	-
Co	0.02-1	15-30	-
Cr	0.1-0.5	5-30	-
Cu	5-30	50-500	6
Mn	20-300	300-500	50
Fe	-	-	100
Ni	0.1-5	10-100	-
Pb	5-10	30-300	-
Se	0.01-2	5-30	-
Ti	-	50-200	-
V	0.2-1.5	5-10	-
Zn	27-150	100-400	20
Zr	-	15	-

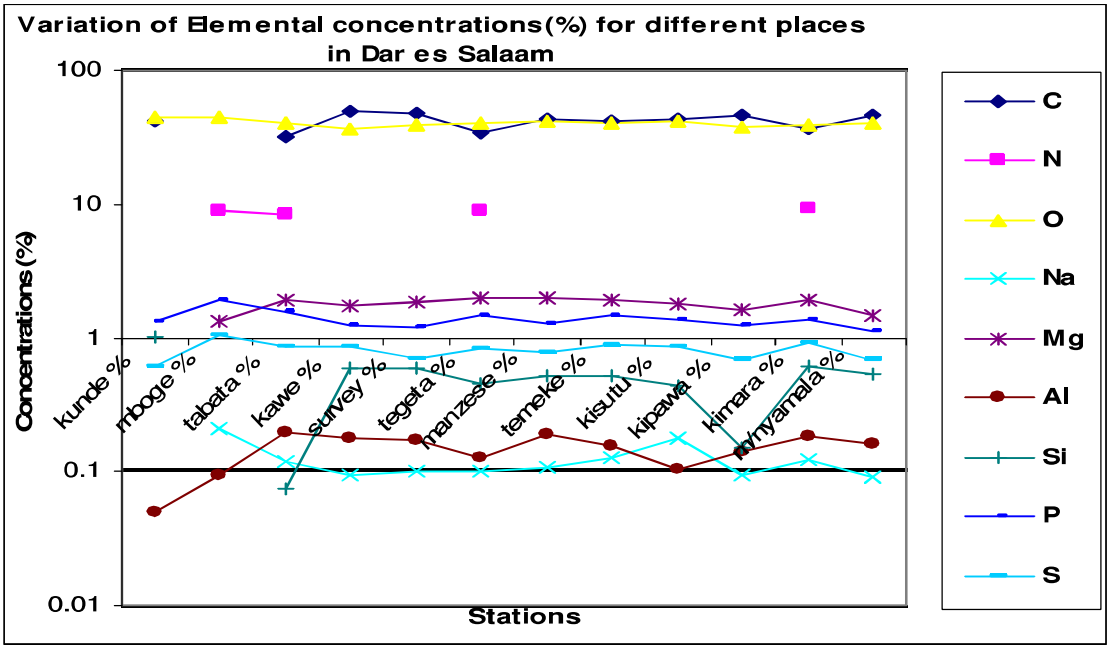


Figure 5. Variation of C, N, O, Na, Mg, Al, Si, P, S in vegetable samples for different stations.

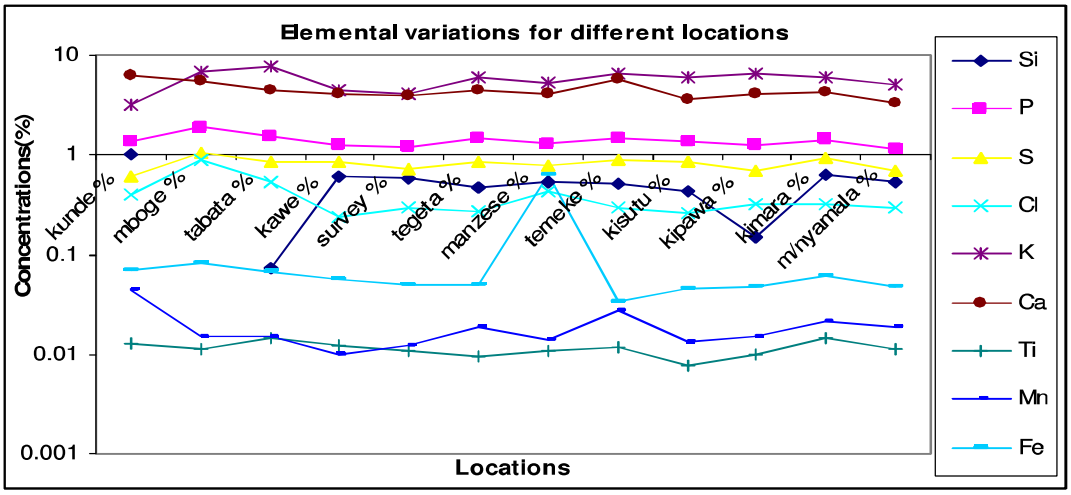


Figure 6. Variation of Si, P, Cl, K, Ca, Ti, Mn and Fe for different stations and kunde and mboga samples.

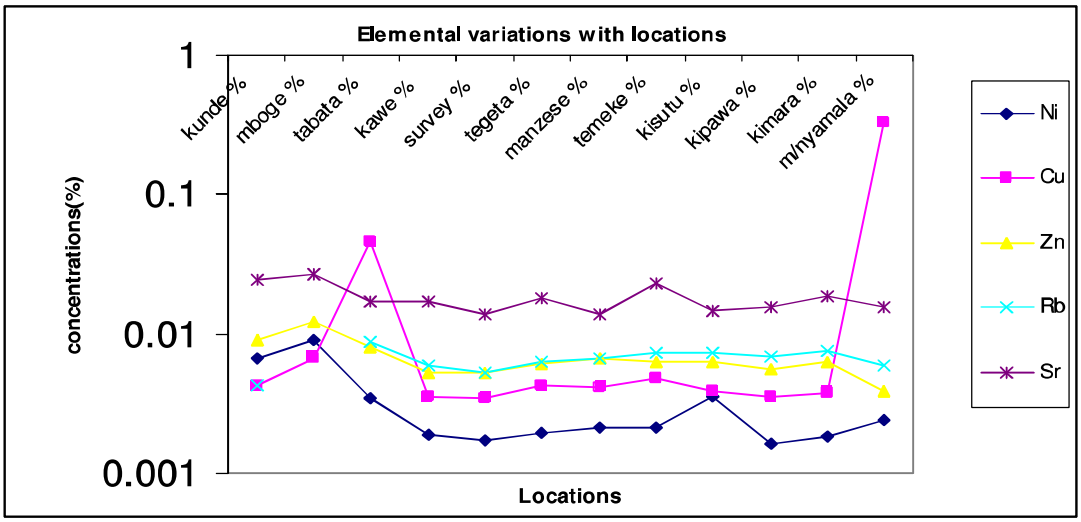


Figure 7. Variation of Ni, Cu, Zn, Rb and Sr for different stations.

stations of sample collection. The same pattern feature observed for Ni, Cu, Zn, Rb and Sr in Figure 7 with shooting of Ni for stations of Kawe and M/nyamala. This could also be due pollution from welding industries in these places

CONCLUSION

Vegetable material grown as food staff in Dar es Salaam have been analyzed by Wavelength dispersive X-ray Fluorescence Analysis (WDXRF) for most of the elements in the material ranging from C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Ni, Mn, Fe, Cu, Zn, Br, Rb, and Sr. The values obtained are within range of those published as essential as foodstuff and thus of high nutrition value. No excessive values have been observed in the results and the toxic elements were either not there or below the detection limits of the equipments. Obviously, the variation in the nutrient levels has been observed for vegetables of different places due to soil fertility or polluted depositions from air, dust, water etc.

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