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Phytochemical Screening and Nutritional Compositions of Onion Bulbs and Tomato Fruits Grown around Arba Minch City, Ethiopia

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ABSTRACT

Though food stuffs considered in this study are important components of human diet, heavy metal contamination in them shouldn't be underestimated for they may pose a risk to human health. Therefore, this study focused on the determination of concentration level of common metals, heavy metals using flame Atomic Absorption Spectrometer, and some nutritional values of onion and tomato samples that were grown in Shelle farm land around Arba Minch City, Ethiopia. As it was observed in the obtained results, the topography of the sampling sites was one of factors affecting the distribution of the metal contents of the samples. The levels of heavy metals were regularly increases in onion samples as it goes from Shelle toward the lake side (Hayk) and irregularities were observed for tomato samples. The obtained results compliment with the acceptable range of WHO guideline.

Keywords: Phytochemical screening; Nutrients; Heavy metals; FAAS; Digestion

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INTRODUCTION

Ethiopia's agro-climatic conditions such as the range of altitude, temperature, soil variability make it suitable for the production of a broad range of agricultural products like fruits (citrus, banana, mango, papaya, oranges, apples), vegetables (cabbages, tomato, cucumbers, pepper, onion, green beans and so on) as well as cut flowers for both home consumption and foreign markets enabling agriculture, to be the major contributor of Ethiopian economy [1].

Fruits and vegetables play a number of important roles in human health because they are considered as "proactive supplementary food" as they constitute significant quantities of minerals, vitamins, carbohydrates; essential amino acids and dietary fibers required for the proper functioning of human metabolic processes and so should be consumed frequently and continuously. They are known to offer anti-oxidative activities in vitamins such as vitamin A, C and E that are important in neutralizing free radicals (oxidants) known to cause cancer, cataracts, heart disease, hypertension, stroke and diabetes [2,3]. They provide foliate and potassium that are known to prevent birth defects,

cancer, heart disease, hypertension and stroke. Furthermore, they are good sources of minerals such as iron, zinc, calcium, potassium, and phosphorus and also contain ample fiber, which is important for digestion and bowel movements [2-4]. Overall, World Health Organization (WHO) places low fruit and vegetable consumption among its twenty risk factors in global mortality, just behind the better known killers such as tobacco use and high cholesterol levels [5]. This indicates that, intake or consumption of high quality vegetables is very important for human health. However, with the development of industrial technology in the present agricultural practice, the increment in diversity and quantities of different chemicals added to agricultural soils to increase crop yields are found to augment the risk of contamination of crops and vegetables [6,7].

The vegetables considered in this study (tomatoes and onions) are part of human meal, that are frequently used in food preparation of household family and themselves, contain trace metals in very minute quantities reached through water used for irrigation, and soil mineralization by crops. Their levels increase as a result of natural rock weathering, waste disposal of car batteries, used metallic household appliances, fertilizers, pesticides, herbicides and industrial effluents [8]. The information of the extent of their uptake and distribution in their body, as well as evaluation of the potential risks in the food chains therefore, should be of a great concern. A lot of researchers worldwide have indeed dealt with the issue and provided relevant information on metal contents of vegetables in general and, onion and tomato varieties along with their growth media mainly water, soil and air in particular. Assessment of levels of heavy metals in onion and other vegetables has been conducted in various countries [9]. Analysis of the proximate composition and energy values of the two varieties of onion (*Allium cepa* L.) was done in Bangladesh and India [10]. Physico-chemical and bioactive properties of onion (*Allium ce*pa L.) seed and seed oil were also studied in Turkey [11]. In Ethiopia, though we share the consequences of global ecological pollution, the issue has not been given a much needed concern and activities towards enhancing societal awareness are far below adequacy. There is study conducted [12] on the status of heavy metals accumulation in some leafy vegetables, grown in Akaki, Kera areas comparing the results with samples collected from Debre Berhan. Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implication in eastern Ethiopia was also studied [13]. Assessment of levels of Lead, Cadmium, Copper and Zinc contamination in selected edible vegetables collected from Bahir Dar town and Adet agricultural research center was conducted [14]. Determination of nutritional profile and physical properties of improved onion (*Allium Cepa* L.) was done [15]. Itanna and his co-workers [16] were worth mentioning on this aspect, particularly on vegetables produced around some areas of Ethiopia. The work includes partitioning and bioavailability of some trace elements in urban vegetable farms amended with municipal wastes at Peacock and Akaki. Effect of drying temperature and duration on nutritional quality of cochoro variety tomato (*Lycopersicon esculentum* L.) was conducted in previous study [17]. Metal concentrations of some vegetables irrigated with waste liquids at Akaki Ethiopia were studied [18]. But yet, there is lack of literature report on the determination of the levels of heavy and common metals in vegetables (tomato and onion) around Arba Minch Town. The present study therefore deals with assessment of phytochemical composition and level of trace metals with determining the concentration of heavy metals; Copper (Cu), Chromium (Cr), Cobalt (Co), Zink (Zn), Cadmium (Cd), Nickel (Ni) and common metals; Sodium (Na), Magnesium (Mg), Potassium (K)

and Calcium (Ca) in edible onion bulb and tomato fruit from Kola Shelle around Arba Minch Town and finally make comparison with FAO/WHO permissible limit.

MATERIAL AND METHODS

Study Area

Kola Shelle is located at 60, 00' 00''North latitude and 370, 34', 59.99'' East longitude in the rift valley of Ethiopia. It is lowland and people use Sego and Sille Rivers to irrigate their farm lands. In summer time the area has an average temperature of 32°C and 22°C in wintertime. People living in the area produce crops like maize and *teff*, vegetables like onion, tomato and green pepper whereas banana, mango and avocado are also known fruits produced there.

Instrumentation

Flame atomic absorption spectroscopy FAAS NOVAA 400P (analytical jena, Germany) equipped with deuterium ark background correctors, hollow cathode lamps for each respective metal, and air-acetylene flame were used for the determination of heavy and common metals.

Reagents and Chemicals

All chemicals and reagents used were of analytical grade reagent unless otherwise stated. Stock Standards of Mg, Ca, Na, Fe, (Bulk Scientific 1-800562-5566 (1000 ppm)), Cu (Hc 69473186), Zn (Hc 60113406 Germany), Cr (Hc 60089979 Germany), Co (Hc 718787850 Germany) were used for preparing the intermediate and series of standard solution for calibration. Nitric acid, 69-72% HNO_3 and perchloric acid, 70% $HClO_4$ were used for digestion of onion bulb and tomato fruit powder samples. Lanthanum chloride hydrate, 99.9 % (Aldrich, USA) was used as a releasing agent for Ca and Mg determination. Distilled-deionized water was used for cleaning apparatus and preparing desired working standard of the metal solutions.

Sample Collection and Preparation

The sampling technique that was used in this research is stratified sampling. The research areas were divided into three places (strata). The vegetable was harvested from each corner of the plots and also from the middle of the plots. Matured onion bulb and tomato fruits samples which appear healthy were freshly collected from each of the three farm sites, pulling out by hand. Samples from each site were combined to make a composite sample of each vegetable per site. Three composite samples of onions (*Allium cepa*) and tomato (*Lycopersicon esculentum*) were collected randomly from each of the three sites. All vegetables were freshly collected and stored in polyethylene bags according to their source (Shelle, Chamo and Hayk) and were brought to the laboratory, kept in a refrigerator for its safety and subsequent preparation.

The collected samples were washed with tap water and rinsed three times with distilled-deionized water. For the analysis, only the edible portions were included, removing bruised or rotten parts. All the samples were chopped into slices with plastic knife and the chopped vegetables were composited and homogenized. The cut pieces were placed in porcelain crucible that was cleaned by washing with acid and rinsed with distilled-deionized water and then dried in hot air. The samples were air dried on white tiles for two days in the laboratory and then oven dried at 60°C for 24 hours to constant weight. The dried onion and tomato samples were pulverized using mortar and pestle

and sieved to obtain fine powder. It was finally stored in screw capped plastic containers and labeled appropriately and placed in refrigerator for analysis.

Sample Digestion for Metal Analysis

There are several digestion procedures available for onion and tomato fruits samples, among that microwave digestion is the best and automated method that was applied in this work using mixtures of different proportions of strong oxidizing agents HNO_3, H_2SO_4 and H_2O_2 as recommended [19] or HNO_3, $HClO_4$ and HCl [20] based on the strength and amount of oxidizing reagents, time, temperature, simplicity, and safety. A weighed amount (0.5 gms) of dried onion bulb and tomato fruit powder were transferred into polytetrafluoroethylene (PTFE) Teflon tube to which 4.0 mL HNO_3 (69-72%) and 4.0 mL $HClO_4$ (70%) were added. The vessel caps secured tightly using a wrench. The complete assembly was irradiated for two hour using Microwave (Top Wave Analytical Jena). Teflon tubes mounted on the microwave carousel were cooled in a water bath for one hour to reduce internal pressure and allow volatilized material to re-stabilize. The digested sample was poured into 50 mL beaker. Distilled-deionized water was used to rinse the PTFE tube and filter through Whatmann 42 filter paper. The solution was transferred were to 50 mL volumetric flask and diluted to the mark with distilled-deionized water. Finally, the digested samples were kept in the refrigerator, for subsequent use.

Optimization of Digestion Procedure

The optimized procedure was selected depending upon: clarity of digests, minimal digestion time, and minimal reagent volume consumption, absence of undigested samples, simplicity and acceptable use of masses of samples. Each digestion trial was dialed three times. Based upon these criteria, the optimal digestion procedure chosen was the one that requires two hour for complete digestion of 0.50 g of onion and tomato powders with 4 mL HNO_3 (69-72%), 4 mL $HCIO_4$ (70%).

Analytical Procedure for Metal Analysis

For the analysis of metals, adjustment of the instrument's operating conditions is an essential part; hence wavelength selection. Slit width and current flow were checked for each metal analyte and the values were recorded in Table 1. To analyze heavy and common metals in vegetables using FAAS NOVAA 400 P (analytical jena, Germany), 10 mg/L intermediate standard solutions were prepared from stock standard solutions (1000 mg/L) for each metal analyte. A series of standard solutions were then prepared for each of metal analyte from the intermediate standard solutions by dilution. The calibration curves obtained were linear for all metals with correlation coefficients higher than 0.995, indicating good relationship between concentration and absorbance. Then the digested samples were directly aspirated into heating chamber and atomized using the air acetylene flame. Finally direct reading of the absorbance was obtained and converted to the concentration unit by comparing with the standard solutions for both heavy and common metals. For common metals, 1% lanthanum nitrate solution was added to the sample as releasing agent to free up the metals. Three replicate reading were carried out for each sample analyte. The same analytical procedure was employed for the determination of elements in digested blank solutions and for the spiked samples.

Procedures for Determination of Proximate Analysis

Total moisture content: Moisture content of a powdered onion sample was determined according to the procedure described in AACC (2000) Method No. 44-15A [10]. It is calculated as follows.

$$\text{Moisture \%} = \frac{(\text{Wt.of original sample} - \text{Wt.of dried sample}) * 100}{\text{Wt.of original sample}} * 100 \quad (1)$$

Crude Proteins

The crude protein content of the considered sample was tested according to the Kjeldahl's method, which involves protein digestion and distillation [15]. The percentage of nitrogen was calculated using the formula:

$$\text{\% Nitrogen} = \frac{(Vs - Vb) * \text{M acid} * 0.0141}{W} * 100 \quad (2)$$

Where, $V_{s.}$=Volume of acid for sample titration; V_b=Volume of acid for blank titration

M_{acid}=Molarity of acid; W=Weight of sample (g).

Then, percentage crude protein in the sample was calculated from the % Nitrogen as % crude protein=% N × F, Where, F (conversion factor 6.25).

Crude Fat

Crude fat was determined by making slight modification on an existing method [10,15]. The % fat in the sample was calculated using the formula:

$$\text{Fat \%} = \frac{\text{Wt.of fat}}{\text{Wt.of original sample}} * 100 \quad \textbf{(3)}$$

Fiber

About 2 g of powdered onion sample was taken into a fiber flask and 100 mL of 0.255 N H_2SO_4 was added. Then the mixture was heated under reflux with heating mantle for one hour. The hot mixture was filtered through a fiber sieve cloth. The difference obtained was thrown off and the residue was returned to the flask to which 100 ml of 0.313 M NaOH was added and heated under reflux for another one hour. The mixture was filtered through a fiber sieve cloth and 10 mL of acetone was added to dissolve any organic constituent. The residue was washed with 50 mL of hot water twice on the sieve cloth before it was finally transferred in the pre-weighted crucible. The crucible with residue was oven dried at 105°C overnight to drive off moisture. The oven dried crucible containing the residue was cooled in a desiccators and latter weighted W_1 for ashing at 550°C for 4 hours [10]. The crucible containing white and grey ash (free of carbonaceous material) was cooled in a desiccator and weighed to obtain W_2. W_3= Weight of sample and % of crude fiber was calculated as follows.

$$\text{Fibe \%} = \frac{W1 - W2}{W3} * 100 \quad (4)$$

Ascorbic Acid

Ascorbic acid content of tomatoes and onion were determined by 2,6-dichlorophenol indophenol titration method described earlier [21]. Accordingly, ascorbic acid content present in the test samples was determined using the formula:

$$Ascorbic\ Acid = \frac{500 * V_2 * 25 * 100}{V_1 * 5 * 5} \quad (5)$$

Where; 500=µg of standard ascorbic acid taken for titration

V_1=Volume of dye consumed by 500 µg of standard ascorbic acid

V_2=Volume of dye consumed by 5 mL of test sample

25=Corresponds to total volume of the extract

5=Weight of sample taken for extraction

5=Volume of the test sample taken for titration

Ash Content

Ash is an inorganic residue remaining after the material has been completely burnt at a temperature of 550°C in a muffle furnace. It is the aggregate of all non-volatile inorganic elements. About 2 g of finely ground dried sample was weighed into a porcelain crucible and incinerated at 55°C for 6 hrs in an ashing muffle furnace until ash was obtained. The ash was cooled in desiccators and reweighed. And then % ash content in the onion sample was calculated as:

$\text{Ash } \% = \frac{\text{weight of ash}}{\text{weight of sample}}$ X 100 [10] (6).

Total Carbohydrate

The total percentage carbohydrate content in the onion sample was determined by the difference method. This method involved adding the total values of crude protein, lipid, crude fiber, moisture and ash constituents of the sample and subtracting it from 100. The value obtained is the percentage carbohydrate constituent of the sample [15].

% carbohydrate=100–(% moisture+% crude fiber+% protein+% lipid+% ash content) (**7)**

Crude Oil

Crude oil was detected by the Soxhlet method by making slight modification on the method used in a previous work [10]. The % fat in the sample was calculated using the formula:

$\text{Fat } (\%) = (\text{weight of fat}/\text{weight of original sample}) * 100$ (8)

Phytochemical Screening

Phytochemical screening of some compounds from tomato fruit and onion bulb sample was done with the method used in the previous work [22] with slight modification.

Statistical Analysis

Statistical analyses were carried out for calculating the mean values, standard deviation, relative standard deviation of each parameter to evaluate the precision and accuracy of the measurement and the correlation coefficients of the calibration curves for the instrument conditioning and calibration. All data were reported as mean ± standard of replicate measurements (n=9).

RESULT AND DISCUSSION

Levels of Heavy and Common Metals

The analyses of metals were conducted following the analytical procedures and their concentration values were given in the Table1.

Chromium: The concentration of chromium in this work was detected and found to be 0.758 ± 0.014, 0.638 ± 0.030 and 0.567 ± 0.014 mg/kg for Hayk, Chamo and Shelle respectively in onion samples. The present value of Cr for onion is higher than reported value of Cr 0.33 ± 0.07 mg/kg [23] and less than 4.5 ± 0.04 mg/kg in [24]. Chromium in tomato samples is found to be 0.506 ± 0.013 mg/kg, 0.526 ± 0.010 mg/kg and 0.304 ± 0.017 mg/kg in Hayk, Chamo and Shelle respectively. The result of Cr in tomato sample is less than the reported value (0.75 ± 0.01) mg/kg [9] and higher than 0.16 ± 0.05 mg/kg [23]. According to WHO (codex almentanius commission, joint FAO/WHO

[25] the safe limit of Cr is (2.3 mg/kg). Therefore, this study indicates that the results of chromium in all samples are below the standard values by WHO and FAO and it is safe to consume tomato fruit and onion bulb of the area.

Table 1. Metal Concentration (mg/kg) in onion and tomato samples (Mean ± S.D)

Metals	Samples					
	Tomato			Onion		
	Shelle	Chamo	Hayk	Shelle	Chamo	Hayk
Cr	0.304 ± 0.017	0.526 ± 0.008	0.506 ± 0.013	0.567 ± 0.021	0.638 ± 0.028	0.758 ± 0.015
Fe	0.063 ± 0.006	0.091 ± 0.036	0.998 ± 0.013	0.618 ± 0.070	0.940 ± 0.090	1.772 ± 0.061
Co	0.056 ± 0.007	0.050 ± 0.007	0.055 ± 0.011	0.048 ± 0.004	0.052 ± 0.009	0.063 ± 0.011
Cu	0.250 ± 0.002	0.301 ± 0.001	0.268 ± 0.002	0.268 ± 0.002	0.269 ± 0.005	0.307 ± 0.007
Zn	1.132 ± 0.094	1.048 ± 0.023	0.420 ± 0.004	0.341 ± 0.009	0.383 ± 0.011	0.592 ± 0.003
Cd	0.039 ± 0.003	0.039 ± 0.001	0.037 ± 0.001	0.038 ± 0.002	0.383 ± 0.011	0.041 ± 0.011
Mg	4.820 ± 0.010	5.060 ± 0.030	5.329 ± 0.036	4.795 ± 0.005	4.830 ± 0.010	4.740 ± 0.036
Na	4.770 ± 0.025	4.860 ± 0.040	4.860 ± 0.040	4.510 ± 0.210	4.750 ± 0.026	4.800 ± 0.026
K	13.21± 0.090	13.23 ± 0.190	13.81 ± 0.300	11.58 ± 0.100	12.47 ± 0.670	11.60 ± 0.160
Ca	3.670 ± 0.250	3.500 ± 0.215	3.950 ± 0.340	3.690 ± 0.135	3.690 ± 0.055	5.095 ± 0.062

Iron: The level of iron in onion bulb in this study is 1.772, 0.940 and 0.618 mg/kg in Hayk, Chamo and Shelle respectively. Report from previous study [26] is 118.15 mg/kg and also with mean range of 30.41 to135.63 mg/kg [27], which are much greater than the present study. WHO/FAO (2001) maximum permissible level of Fe in vegetables was 450 mg/kg [12]. As described [28] WHO/AOAC safe limit of Fe in vegetable was (1.3 mg/kg). When compared with the standard value the result of this work is below the safe limit. Tomato has Fe concentration of 0.618, 0.091 and 0.063 mg/kg, in Hayk, Chamo and Shelle respectively. Similar study conducted [9] show that the Fe concentration is 6.444 ± 1.8 mg/kg and other research work [29] reported 5.09 to 6.38 mg/kg of Fe concentration, which is higher than its concentration found in the current study.

Copper: In this study Cu amount is determined and reported as the mean value of copper in each sample and found to be 0.268 mg/kg, 0.269 and 0.307 mg/kg in Shelle, Chamo and Hayk onion bulb respectively. When compared with the results from previous studies the current amount obtained is lower than 0.437 mg/kg in [9] and 7.00 mg/kg [8] and11.4 ± 0.64 mg/kg. In the same way the concentration of copper in tomato fruit determined and reported in Shelle, Chamo and Hayk samples are 0.2501, 0.2683, and 0.301 mg/kg respectively. The reports from previous works [8] having mean value of 5.57 ± 0.98 mg/kg, [28] with the amount of 8.427 ± 0.635 mg/kg and [23] from non-polluted environment having value 0.51 ± 0.15 mg/kg show higher concentration of copper than the current result of copper in tomato samples from the three sites of the study area. The present result was also compared with international standards FAO/WHO and found to be less than the safe limit (5.0 mg/Kg) that cited by standards [8]. The comparison with international standards shows that the level of the metal in each sample is in the safe limit. Therefore consuming onion and tomato products of this area is safe for human health.

Cobalt: The mean concentration of Coin onion samples of this study was 0.048, 0.052 and 0.063 mg/kg in Shelle, Chamo and Hayk respectively, and in tomato its level is 0.0564, 0.050 and 0.055 mg/kg in Shelle, Chamo and Hayk

respectively. When the current result of Co in onion determined is compared with mean values 0.51 ± 0.023 [30] and 0.17 ± 0.05 mg/kg [21] the current study has lower amount. The tomato results found in this study is also lower than 0.45 ± 0.01 [31] and 0.13 ± 0.09 mg/kg [23] reported previously. WHO/FAO maximum level of Co, in vegetables is 0.5 mg/kg [30] and the result in the present study is less than the permissible level in the standard.

Zinc: The concentration of Zn in onion sample is 0.341, 0.383 and 0.592 mg/kg in Shelle, Chamo and Hayk, and Zn in tomato is 1.132, 1.048 and 0.592 mg/kg in Shelle, Chamo and Hayk respectively. The present work has lower level of zinc in onion samples when compared with the previously reported result 11.4 ± 0.64 in [30], 2.19 ± 0.258 [14] and 2.80 mg/kg [30]. The result of Zn in tomato samples obtained is also lower than 8.427 [28], 3.902 ± 0.012 [14] and 4.52 ± 0.05 mg/kg [24]. According to a study [28] WHO maximum permissible level of Zn is 100 mg/Kg indicating lower than permissible limit, therefor the consumption of these vegetables can be considered safe with no risk to human health.

Cadmium: In this study the Cd amount is determined and reported as the mean value of Cd in each sample and found to be 0.038, 0.035 and 0.041 mg/kg in Shelle, Chamo and Hayk onion samples respectively. Comparing the current Cd value with the results from previous studies of similar samples, the current amount obtained is lower than 0.120 ± 0.011 mg/kg reported [14].

The concentrations of Cd in tomato fruit samples of the three farm sites are 0.039, 0.039 and 0.037 mg/Kg in Shelle, Chamo and Hayk. The concentration of Cd found in tomato sample of this work is lower than that of previous works 0.115 ± 0.025 [14] and 0.96 mg/kg [26]. When it is compared with the standard values cited by WHO and FAO [24] (0.02 to 0.2 mg/kg), the level of Cd in all onion and tomato samples of the current study is found to be in the safe limit and it is also in safe limit comparing with European Union (EU) 0.2 mg/kg as described [32]. This indicates that onion bulbs and tomato fruits of the area are not contaminated by Cd metal.

Sodium: In this study the Sodium amount was determined and reported as the mean value of Sodium in each onion bulb and tomato samples. Its amount in onion bulb is found to be 4.51 ± 0.21, 4.75 ± 0.026 and 4.8 ± 0.026 mg/kg in Shelle, Chamo and Hayk farm sites respectively. There is reports from previous as 30.36 mg/kg [31], showing that the amount obtained in the current study is lower than the literature value. Similarly Na in tomato fruit sample is detected and reported as 4.77 ± 0.025, 4.86 ± 0.040 and 4.88 ± 0.110 mg/kg for Shelle, Chamo and Hayk farm sites respectively. Comparing with literature value, the concentration of Na in tomato sample is found to be lower than the reported value 40.0 mg/kg [33].

Potassium: The concentration of potassium in this work is determined and it is 11.58 ± 0.10, 12.47 ± 0.67 and 11.60 ± 0.16 mg/kg in Shelle, Chamo and Hayk respectively. The mean concentration of K in tomato samples of this study is 13.21 ± 0.090, 13.23 ± 0.190 and 13.81 ± 0.30 mg/kg in Shelle, Chamo and Hayk respectively. In this work the amount of potassium in both vegetables is lower than 1460 mg/kg reported in the literature [33].

Magnesium: The concentration of Mg in onion sample of the current work in Shelle, Chamo and Hayk farm sites is 5.1, 5.2 and5.7 mg/kg respectively. The mean concentration of Mg in tomato fruit samples of this study is 5.63, 5.698 and 5.6 mg/kg is found from Shelle, Chamo and Hayk, study areas. The current result of Mg in tomato sample was much less than 100 mg/kg in reported literature [33].

Calcium: The amount of Ca determined and reported in onion bulb sample of this study was 3.69 ± 0.13, 3.69 ± 0.055 and 5.095 ± 0.062 mg/kg in Shelle, Chamo and Hayk respectively. Results of Ca in tomato fruit shows that 3.67 ± 0.25, 4.86 ± 0.040 and 4.88 ± 0.110 mg/kg when compared with previous work 230 mg/kg [33], the current study has lower value of Ca in both tomato and onion samples.

Table 2. Metal contents of onion samples with the instrumental precision (%RSD, n=9)

Metal	Mean ± SD in mg/kg			%RSD		
	Shelle	Chamo	Hayk	Shelle	Chamo	Hayk
Chromium	0.57 ± 0.02	0.64 ± 0.03	0.76 ± 0.02	3.5	4.7	2.6
Iron	0.69 ± 0.07	0.94 ± 0.09	1.77 ± 0.06	10.1	9.6	3.4
Cobalt	0.05 ± 0.004	0.06 ± 0.01	0.06 ± 0.01	8	16.7	16.7
Zinc	0.342 ± 0.01	0.38 ± 0.01	0.59 ± 0.003	2.9	2.6	0.5
Copper	0.270 ± 0.002	0.27 ± 0.01	0.301 ± 0.001	0.7	0.7	0.3
Cadmium	0.040 ± 0.002	0.039 ± 0.003	0.040 ± 0.001	5	7.7	2.5
Magnesium	4.80 ± 0.01	4.83 ± 0.01	4.74 ± 0.04	0.2	0.2	0.8
Sodium	4.51 ± 0.21	4.75 ± 0.026	4.8 ± 0.026	4.7	0.6	0.5
Potassium	11.58 ± 0.10	12.47 ± 0.67	11.60 ± 0.16	0.9	5.4	1.4
Calcium	3.69 ± 0.135	3.69 ± 0.055	5.095 ± 0.062	3.7	1.5	1.3

Precision of Analytical Method

Precision is as a measure of the closeness (degree of scatter) between independent test results obtained under stipulated conditions (stipulated conditions can be, for example, repeatability, intermediate precision, or reproducibility). The required precision was determined by the role of the test results that it is going to play in making a decision. Precision is usually expressed numerically by measures of imprecision, such as standard deviation (less precision is reflected by a larger standard deviation) or relative standard deviation of replicate measurements [34].

In the current study, the precision of the method was evaluated by calculating the relative standard deviation (RSD) of the triplicate samples with triplicate reading of 9 total measurements (n=9). The values of RSD from the obtained result were within the acceptable range of the analytical standard, which are less than 10 for all analytes except for cobalt. Therefore, we can say that the method is in the acceptable working condition in terms of precision and the results of the metal contents of onion and tomato samples were given in Tables 2 and 3 respectively.

Method Validation

Trueness is determined by using certified reference materials or comparing the new method with a reference method or performing a spike-and-recovery experiment. Trueness of all elements was determined through a spike-and-recovery experiment in which a known amount of analyte is added to the sample matrix [9]. This method is used to determine whether a systematic shift occurs in the analytical signal of an analyte due to matrix effects. In this study, in order to confirm the trueness of the complete method including digestion and the measurement, a spike and recovery test was used.

In order to ascertain the accuracy of optimized wet digestion procedure, recovery tests were performed using spiked samples with known concentration. Accordingly, known amounts (2 mg/L) is prepared for each metal element and spiked on 0.5 g solid samples. The spiked and non-spiked samples were digested in parallel using the optimized,

microwave digestion procedure and concentration of each metal was determined in triplicate samples by taking three reading for each metal with total of 9 measurements and the results were presented in Table 4 for onion samples respectively. Using equation 8, the results of percentage recoveries for the studied metal ranged for all metals between 88.50-99.50 %, showing the acceptable range.

Table 3. Metal contents of tomato samples with the instrumental precision (%RSD, n=9)

Metal	Mean ±SD in mg/kg			%RSD		
	Shelle	Chamo	Hayk	Shelle	Chamo	Hayk
Chromium	0.30 ± 0.02	0.53 ± 0.01	0.51 ± 0.01	6.7	1.9	2
Iron	0.063 ± 0.006	0.091 ± 0.004	1.00 ± 0.01	9.5	4.4	1
Cobalt	0.06 ± 0.01	0.050 ± 0.007	0.06 ± 0.01	16.7	14	16.7
Zinc	1.13 ± 0.09	1.05 ± 0.02	0.420 ± 0.004	8	1.9	1
Copper	0.250 ± 0.002	0.301 ± 0.001	0.268 ± 0.002	0.8	0.3	0.7
Cadmium	0.039 ± 0.003	0.388 ± 0.007	0.037 ± 0.001	7.7	1.8	2.7
Magnesium	4.82 ± 0.01	5.06 ± 0.03	5.33 ± 0.04	0.2	0.6	0.8
Calcium	3.67 ± 0.25	3.50 ± 0.22	3.95 ± 0.34	6.8	6.3	8.6
Sodium	4.77 ± 0.03	4.86 ± 0.04	4.88 ± 0.11	0.6	0.8	2.3
Potassium	13.21 ± 0.09	13.23 ± 0.19	13.81 ± 0.30	0.7	1.4	2.2

Determination of Proximate Analysis

The nutritional values of both onion and tomato samples were determined using different recommended methods and presented in Table 5.

Moisture content in this work refers to the amount of free water and volatile substances that are lost by drying the vegetable under controlled temperature in an air oven. Moisture value of onion bulb and tomato fruit range from 4.8 ± 0.13 to 6.40 ± 0.51% and 5.6 ± 0.2 to 6.38 ± 0.2% respectively. The value for onion bulb is slightly higher and that of tomato fruit is close to the values reported in the literature [17].

The ash content for this work ranges from 9.6 ± 0.05 to10.5 ± 0.07% for onion and 8.9 ± 0.07 to 9.94 ± 0.05% for tomato in the three study areas. The trend of the value indicates that, for onion Shelle<Chamo<Hayk and for tomato, Shelle<Hayk<Chamo. Comparing these results with the results of the previous work 4.44 ± 0.1% [15] and 7.34 ± 0.5% [35] for onion and 4.14 to 8.3% [15] for tomato, the present results are higher.

Protein content for this study are 5.34 ± 0.2 to 5.21 ± 0.07% for onion and 8.77 ± 0.104 to 8.62 ± 0.076% for tomato. The literature values of the species are 10.84 ± 1.23% [15], 15.62% [36], 3.90% [37] for onion and 5.60% [15] for tomato which shows that, the present result is slightly less for onion and greater for tomato than literature values. Therefore, consumption of both onion bulb and tomato fruit of the area is feasible to obtain protein.

Carbohydrate level of onion ranges between70.79 and 72.25% for the areas selected. This value is greater than the previous literature value 21.56% [15] and is comparable with the other work 69.48% [36].

The amount of carbohydrate in tomato fruit falls between 66.99 and 69.05%, which is greater than reported value 60.15% [17]. This indicates that nutrition from this area is rich in carbohydrate.

Table 4. Recovery Tests for the optimized procedure

Metal	Onion Sample	Concentration of spiked sample (mg/kg)	Concentration of non-spiked sample(mg/kg)	% Recovery
	Shelle	2.500 ± 0.028	0.57 ± 0.02	96.6
	Chamo	2.513 ± 0.019	0.64 ± 0.030	93.76
Chromium	Hayk	2.612 ± 0.032	0.76 ± 0.01	92.71
	Shelle	2.585 ± 0.034	0.62 ± 0.05	98.37
	Chamo	2.785 ± 0.053	0.94 ± 0.02	92.24
Iron	Hayk	3.655 ± 0.025	1.77 ± 0.07	94.1
	Shelle	1.862 ± 0.010	0.048 ± 0.004	91
	Chamo	1.850 ± 0.0042	0.05 ± 0.01	89.9
Cobalt	Hayk	1.900 ± 0.009	0.06 ± 0.01	91.8
	Shelle	2.085 ± 0.0003	0.270 ± 0.002	90.86
	Chamo	2.090 ± 0.001	0.27 ± 0.01	91.05
Copper	Hayk	2.153 ± 0.001	0.307 ± 0.001	92.29
	Shelle	1.850 ± 0.002	0.040 ± 0.01	90.5
	Chamo	1.798 ± 0.003	0.039 ± 0.0045	87.4
Cadmium	Hayk	1.801 ± 0.0109	0.040 ± 0.01	87.98
	Shelle	2.267 ± 0.0078	0.341 ± 0.002	96.3
	Chamo	2.31 ± 0.002	0.383 ± 0.011	96.39
Zinc	Hayk	2.501 ± 0.006	0.592 ± 0.003	94.79
	Shelle	6.655 ± 0.05	4.795 ± 0.005	93
	Chamo	6.696 ± 0.010	4.803 ± 0.010	93.6
Magnesium	Hayk	6.62 ± 0.035	4.94 ± 0.036	94
	Shelle	5.57 ± 0.135	3.69 ± 0.05	94
	Chamo	4.900 ± 1.170	3.69 ± 0.005	94.6
Calcium	Hayk	6.971 ± 0.002	5.09 ± 0.062	93.8
	Shelle	6.41 ± 0.21	4.51 ± 0.21	95
	Chamo	6.69 ± 0.212	4.75 ± 0.026	97
Sodium	Hayk	6.76 ± 0.23	4.8 ± 0.026	98
	Shelle	13.58 ± 0.10	11.58 ± 0.10	99.5
	Chamo	14.71 ± 0.67	12.47 ± 0.67	98
Potassium	Hayk	12.89 ± 0.159	16.60 ± 0.16	97.8

The crude fat of onion bulb of present study is in the range of 2.50-1.84% that is more than the value reported 0.1% [2], and the level of crude fat in tomato fruit in the current study is in the range of 4.7-3.86% which is higher than the amount reported in literature 1.61% [36].

The content of fiber for this study is 5.30 to 5.45% for onion. The value of fiber reported [15] in previous work is between 2.58 to 5.15% in different onion varieties. The result indicates higher value of fiber in for work. The content of fiber in tomato fruit is between 2.98 to 4.21% that was less than the value 4.71 to 9.63% reported [17]. Therefore, onion and tomato products of the area are rich in fiber.

Ascorbic acid levels are 2.875 ± 0.125, 2.5 ± 0.125 and 2.216 ± 0.118 mg/100 g for Shelle, Chamo and Hayk onion bulb respectively. The ascorbic acid in onion bulb in previous work, 7.54 ± 0.99 [22] is higher than result of the present study. The value in tomato is 1.94 ± 0.06, 1.81 ± 0.07 and 1.475 ± 0.213 mg/100 g respectively for Shelle, Chamo & Hayk.

Table 5. Some nutritional values of onion and tomato sample (mean ± SD)

Parameter	Onion sample			Tomato Sample		
	Shelle	**Chamo**	**Hayk**	**Shelle**	**Chamo**	**Hayk**
% Moisture	4.8 ± 0.13	5.2 ± 0.3	6.40 ± 0.51	5.6 ± 0.2	6.01 ± 0.20	6.38 ± 0.2
% Ash	9.6 ± 0.05	10.0 ± 0.05	10.5 ± 0.07	8.9 ± 0.05	9.2 ± 0.07	9.94 ± 0.07
% Crude oil	2.5 ± 0.015	2.31 ± 0.03	1.8 ± 0.03	4.7 ± 0.036	4.16 ± 0.04	3.86 ± 0.06
% Crude protein	5.34 ± 0.2	5.23 ± 0.1	5.21 ± 0.07	8.77 ± 0.104	8.60 ± 0.07	8.62 ± 0.076
% Crude fiber	5.51 ± 0.076	5.43 ± 0.076	5.30 ± 0.076	2.98 ± 0.04	3.36 ± 0.07	4.21 ± 0.08
% Carbohydrate	72.25	71.83	70.79	69.05	68.67	66.99
% Ascorbic acid	2.875 ± 0.125	2.5 ± 0.125	2.216 ± 0.12	1.94 ± 0.06	1.81 ± 0.07	1.47 ± 0.213

Phytochemical Screening

The phytochemical screening was conducted to test the presence or absence of the metabolites that are responsible for medicinal values of the plant content by using different chemical testing mechanisms and the results were presented in Table 6.

Table 6. Phytochemical test results

Test Parameters	Onion samples			Tomato Samples		
	Shelle	**Chamo**	**Hayk**	**Shelle**	**Chamo**	**Hayk**
Alkaloid test						
Dragendorff's test	++	+	++	+	+	+
Meyers reagent	+	-	-	+	+	+
Wagner's reagent	+	+	+	+	+	+
Flavonoid test	-	-	-	-	-	-
Phenolic test	-	-	-	-	-	-
Tannin test	-	-	-	-	-	-

++ = highly Present, + = present, - = absent

The phytochemical screening results obtained in this work show that the qualitative identification of some phytochemicals like, Flavonoid, Phenolic and Tannin show negative test in all onion and tomato samples and Alkaloids are absent in onion samples for Chamo and Hayk according to Mayer's test. The test results show positive result for alkaloids according to Dragendorff's and Wagner's test for both onion bulb and tomato fruit.

CONCLUSION

The levels of heavy and common metals in onion bulb and tomato fruit samples collected from the area of the study were determined. Some heavy metals show little increment as it goes to the lake side of the sampling site in onion

bulb but irregular in case of tomato samples. The obtained results of all heavy and common metals were compared with the values cited by WHO guideline and it was found to be within the permissible limit (below the maximum permissible values) of the guideline. Therefore, it gives the confidence for the user to eat these vegetables as it is free of those selectively determined heavy metal contents. The proximate analysis and phytochemical screening were also done and discussed. These values give information about the medicinal values of the both samples.

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