

Determination of Heavy Metals Concentration in Four Different Samples of Apples Distric Kalat, Balochistan, Pakistan¹

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Abstract

Various elements, as well as heavy metals, found in various natural fruits, play vital roles in the lives of humans. In order to test this hypothesis, the amounts of five distinct elements, including heavy metals, were measured in a various types of apples. For the mineralization of apples materials, a wet digestion approach was used using three strong acids, sulphuric acid (H_2SO_4), nitric acid (HNO_3), and per chloric acid ($HClO_4$), in a ratio of 1:5:0.5 ml, followed by filtration and analysis using flame atomic absorption spectroscopy. For K, a flame photometer was used, with samples diluted up to a hundred fold to get readings within the instrument's range. Fe, Cu, Pb, Ni, and K are the ascending order of element concentration in apples. According to the research, the concentration of heavy metals accumulated in apples was different. Furthermore, the concentrations were within an international organization's established range.

Keywords: Metals, Apples, Atomic Absorption Spectrophotometer, Flame Photometer

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INTRODUCTION

Fruits are well-known for containing vital components that the human body need, such as polysaccharides, carbohydrates, vitamins, minerals, and organic acids [1]. Fruits are also beneficial in the treatment of a variety of human ailments due to the presence of antioxidants and other biologically active components [2]. As a result, fruits are an important part of the human diet, and locals are gradually increasing their fruit consumption. On the other hand, because poisoning of the food chain is one of the most serious problems,

Food safety has been a major public concern across the globe in last few years [3, 4]. It's one of the most common ways for harmful chemicals to enter the body. Because heavy metals are one of the most common pollutants, heavy metal contamination in fruits has become a serious issue in people's everyday diets [5].

High amounts of heavy metals have been linked to fruits like mangoes, strawberries, grapes, cherries, apples, melons, oranges, and bananas [6]. Heavy metal contamination of fruits is caused by irrigating with contaminated water, using metal-based insecticides and fertilisers, and other reasons. Cu concentrations in fruit have been demonstrated to rise after long-term use of Cu-based fungicides in apple orchards [7].

Elements that aren't required for plant growth but can have an impact on crop output, animal welfare, and human health are becoming more significant. Micronutrients or trace elements, such as zinc, nickel, and manganese, play an important role in plant growth. If products are to be regulated at a high-efficiency production level, determining the necessary elements present in plants, soil and fruits [8]. Metallic and non-metallic elements are required by the human body in order to maintain good health. As a result, knowing the elemental composition of edible plants and food is required to understand their therapeutic value [9-10]. A total of 92 elements can be found in nature. Humans are poisoned by almost 30 metals and metalloids. Transition metals, lanthanides, and actinides are all heavy metals [11]. Heavy metal ions are absorbed through the root system and begin to deposit on various parts of the plant, resulting in a reduction in plant development. Heavy metals are not poisonous at

low concentrations, but they cause harm to the human body when concentrations approach a critical level. Pb is one of the most plentiful heavy metals on the surface of the world [12]. Heavy metals, with the exception of natural disasters, are examples of environmental pollutants. The anthropogenic activities include the adverse effects of heavy metals on the environment [13]. Many plant species have been used for numerous infectious diseases ranging from minor infection to dangerous ailments like skin, asthma and horde of indication [14]. Because these are non-biodegradable toxic chemical species, determining the total concentration of metals cannot provide entire information about their forms. However, finding heavy metals that are different from other metals can provide complete information about their forms [15].

Because of its high specificity, low detection limit, simplicity of use, and ease of sample preparation, atomic absorption spectroscopy (AAS) is a useful approach for the measurement of trace elements [16]. AAS is extremely sensitive, and it can determine the concentration of many elements at very low levels [17]. We analyse the interaction of electromagnetic radiation (EMR) with a sample and then measure the attenuation of EMR intensity in spectroscopy [18]. As the number of atoms of the selected element in the light path rises, the amount of light absorbed at that wavelength increases, and so is proportional to the element's concentration [19].

The province of Balochistan Pakistan's leading fruit grower, earning it the moniker "Fruit Basket of Pakistan" for its annual apple production of 224000 tonnes. Apple is responsible for over 23% of total production in the country [20]. The highlands of Balochistan produce apples in the districts of Mastung, Kalat, Quetta, Pishin, Ziarat, Killa Abdullah, Killa Saifullah, Loralai, and Zhob. However, this research is mostly focused on a few specific apple samples, and little is known about heavy metal accumulations and distributions in different varieties of apples (fruits) on a regional basis of District kalat Balochistan. A regional-scale understanding of heavy metal accumulations in apples is useful for mapping the distribution, tracing potential sources, and evaluating the eutrophication risk.

MATERIALS AND METHODS

Reagents and Solutions

For the analysis of heavy metals, Merck, Marker purchased various analytical grade standards (1000 ppm) of metals (Fe^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , and K). These metals' working standard solutions (0.1–20 ppm) were made by diluting the relevant aliquots from their stock solutions with a 1:5:0.5 mixtures of H_2SO_4 , HNO_3 , and HClO_4 . The acids H_2SO_4 , HNO_3 , and HClO_4 were used in a ratio of 1:5:0.5 for fruit (Apple) digestion. This mixture was made up of analytical-grade stock solutions of these acids that were commercially accessible.

Instruments and Glassware's

With hollow cathode lamps of various metals and an air-acetylene flame, an atomic absorption spectrophotometer (Thermoelectron S4 AA) was utilised to determine heavy metals. By using a flame emission spectrophotometer, K was analysed in the mentioned fruit (Apple) by using an instrument Flame Photometer (Jenway PFP7). Round bottom flasks, conical flasks, and pyrex glass beakers were utilised. Pre-cleaning with surfactant was followed by soaking in HCl bath (10 % v/v) for a week and rinsing with deionized water numerous times.

Sample Collections

Apple fruits of various types, termed Kaja, Tor Kulu, Amri, and Shin Kulu, were obtained in fresh condition from various places of district Kalat of Balochistan. Agriculture Research Department, Sariyab Road, Quetta, identified the apple varieties.

Sample Preparation

After drying, the apples were ground into powder using an electrical blender, which was then used for AAS and flame photometer analysis. The powdered fruits were digested using a technique [21] that had previously been published. In a 50mL round bottom flask, 0.25g powder of each fruit (apple) was added, followed by 6.5mL acid mixture (5mL nitric acid, 1mL sulphuric acid and 0.5mL per chloric acid). These acids were extracted from stock solutions that are commercially accessible. Each fruit sample containing a mixture of

acids was cooked on a hot plate (JENWAY 1000) at 80–85 degrees Celsius until white vapours emerged from the flask. The presence of these white vapours indicates that digestion is complete. Following that, a few drops of distilled water were poured to it, and it was taken off the hot plate for around 5–10 minutes to cool. The digested mixture was then transferred to a 50mL volumetric flask and filled with distilled water, followed by filtration using Whatmann No.42 filter paper in marked plastic bottles. After wet digestion, these produced solutions were examined for element detection using an AAS and a flame photometer. For the purpose of calibration, dilutions of various concentrations were generated from analytical grade stock standards of 1000 ppm. These dilutions were made right before the samples were run. Throughout the project, deionized water was used. The technique was used to assess potassium using (Jenway PFP7's) FES. The samples were diluted 100 times with deionized water in order to achieve results within the flame photometer's range.

RESULTS AND DISCUSSION

Results

The acquired results for Fe²⁺, Cu²⁺, Pb²⁺, Ni²⁺, and K are displayed in Table 1. However, the comparison among the metals is indicated in figure 1 and 2.

Table 1: Concentration of heavy metals in different varieties of Apples.

Samples	Metals (ppm)				
	Fe ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	K
Shin Kulu	0.5666	0.1912	0.0152	0.1046	584.151
Kala Kulu	4.3499	0.2323	0.01547	0.0885	556.16
Kaja	0.3311	0.3894	0.0418	0.1025	608.8
Amri	0.5662	0.2322	0.2323	0.1109	584.150

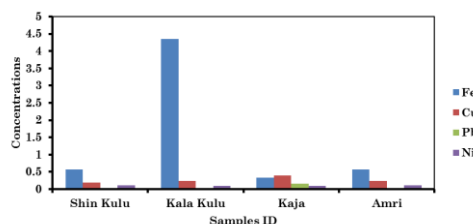


Figure 1: Comparison of Concentration of heavy metals

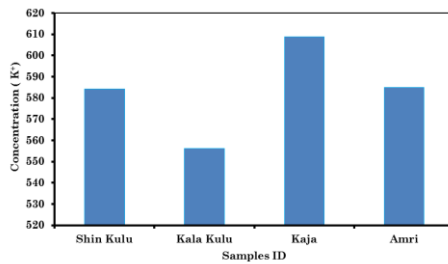


Figure 2: Comparison of Concentration of Potassium

DISCUSSION

Because of its accuracy, AAS is commonly used to estimate various heavy metals. Furthermore, flame emission spectroscopy is a straightforward approach for determining sodium and potassium concentrations. Samples of K were produced using the dilution procedure with deionized water, with the range of calibration curves of different elements taken into account. Because AAS is linked, Disputes (ppm). When computer equipment detects multiple elements, it calculates their concentrations, whereas a flame photometer cannot. As a result, the potassium concentrations were computed using a regression equation. The mineralization of fruit materials was achieved with satisfactory results using the wet digestion method. By employing strong oxidising agents, this process eliminates the organic components that surround the minerals, leaving only the minerals in an aqueous solution. Other digesting procedures, such as dry ashing and microwave digestion, are more complicated and time-consuming.

In the human body, iron is required for the production of red blood cells. Iron deficiency in the human body causes anemia [22]. Because of the high iron content, human bodily tissues are damaged [23]. According to the WHO, the maximum amount of iron that can be consumed by plants is 20mg/kg, whereas humans can consume between 10 and 28mg per day [24]. As comparing the results which are given in the Table No 01 the sample kala kulu having a highest concentration of Fe^{2+} 4.34 ppm and other mean iron contents of 0.5666 ppm, 4.3499 ppm, 0.3311 ppm and 0.5662 ppm, respectively.

The average total Cu content of soil beneath 3-year old apple trees was 11.86 ppm. The soil beneath 15-year-old apple

trees had a value of 18.43 ppm, while the soil beneath 15-year-old apple trees had a value of 18.43 mg kg⁻¹. As a result, with long-term fruit tree planting, modest increases in soil heavy metal concentration should be expected, and heavy metal pollution levels in orchard soils should be quantified on a regular basis. The outer tissues of all fruit samples had higher heavy metal contents than the inner tissues. The varying accumulation abilities of different organs, the initial spray deposit and retention of pesticides, and probable air deposition could all be factors in these phenomena. Furthermore, the presence and use of Pb (Lead) distinguishes it from other heavy metals in terms of environmental toxicity, which is why it is critical to research heavy metals such as Pb (Lead). Furthermore, the maximum copper concentration in plants is 10 ppm, which is reduced to 2–3 mg per day for human consumption [25]. Cu concentrations were 0.19120 ppm, 0.2323 ppm, 0.3894 ppm, 0.2322 ppm, respectively.

Nickel is essential for the creation of insulin in both humans and plants in extremely small amounts. Its deficiency, on the other hand, causes liver damage. It is harmful in high concentrations and causes a variety of illnesses, including heart disease, weight loss, and liver issues. The permitted limit of Ni in plants is 1.5 mg/kg, while the food intake limit is 1 mg/day, according to the WHO [26]. Ni found concentrations in apple samples 0.1046 ppm, 0.0885 ppm, 0.1025 ppm, and 0.1109 ppm respectively.

Lead is a heavy metal component; it is stored in the bones and teeth, causing stiffening and hardening of the bones, as well as limb and wrist weakness. Lead poisoning impairs the activities of the body's soft tissues, kidneys, immunological, reproductive, and nervous systems. The maximum amount of lead that may be consumed safely by humans is one gram. Lead consumption is limited to 1.5 ppm in humans [26]. In the apples samples the average lead concentrations were 0.0152 ppm, 0.01547 ppm, 0.0418 ppm and 0.2323 ppm respectively. Potassium helps regulate hormones, insulin secretion, and immune system responses. Potassium aids in blood pressure reduction. It's used to treat liver and renal issues. Potassium intake limits for women and men are 2300 mg per day and 3100 mg per day, respectively [28]. K concentrations were 584.15 ppm, 556.16 ppm, 608.8 ppm and 584.150 ppm, is respectively.

CONCLUSION

The concentration of heavy metals in Fruits (Apples) found within the safe limits set by international organisations like the FAO and the WHO, according to this study. There were five elements assessed, both necessary and non-essential. Potassium concentrations were found to be higher in all samples, although heavy metal concentrations were within permitted values. Heavy metal contamination levels for (Fe, Cu, Pb, Ni) was found very in all samples except the concentration of Fe in sample Kala Kulu which is quit high as comparing with other sample and WHO limit ranges and majority of them The non-polluting values of the Apples were high. Furthermore, risk assessments based on the results of apple flesh samples demonstrated that eating apples from the Cu Zn Cr Cd examined areas did not pose any health hazards. Metal determination that is accurate and precise is quite important.

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