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Determination of the Concentration of Some Heavy Metals in the Pulp and Peel of Some Citrus Fruits Using Atomic Absorption Spectrometry

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ABSTRACT

Heavy metals that are derived from the markets of Anbar Governorate, Iraq, including oranges, tangerines, lemons, Sindhi, and grapefruits. After cleaning and drying, the samples were subjected to digestion with concentrated hydrochloric and nitric acids. The concentrations of iron, chrome, nickel, copper, cadmium and lead were then determined using atomic absorption spectrometry. While most minerals were within the international authorized range of 0.1% to 0.3%, as determined by the FAO/WHO, some citrus types had concentrations that were greater than this range. Statistical analysis was employed to interpret the results. The results of the study demonstrated that the majority of the observed concentrations of all of the minerals examined were less than the maximum allowable concentrations, which were set by the FAO/WHO. As a result, these minerals are considered safe to consume. However, some minerals were documented to be present in some citrus plants that were gathered from the markets of Anbar Province exceeding the authorized limits.

1. INTRODUCTION

Citrus fruits are flora that are wealthy in nutrition C, phytochemicals, and fiber. Most sorts are very low in calories. As for acidity, citrus culmination can range in acidity. Some citrus culmination, such as yellow lemons and green lemons, are very acidic and difficult to consume on their own. However, different types, such as oranges and tangerines, are very sweet [1], and in case you choose citrus fruits, they ought to be firm and extremely heavy for their length. Of these results [2-4], lemons (citrus fruits) are frequently utilized in traditional treatments because of their excessive content material of crucial vitamins and antioxidants. They are recognized for their position in getting rid of free radicals, that could harm human cells. Such as: diet C, folate, and potassium. Grapefruit: Grapefruit is one of the fruits that enables decrease insulin degrees and may assist lessen the threat of kidney stones in humans with kidney problems. Oranges: The evergreen tree, normally acknowledged for its orange fruit, is rich in antioxidants and vital micronutrients such as vitamin C, folate, and potassium. Regular consumption of oranges has many health benefits, which include progressed heart health, reduced inflammation, and a reduced hazard of kidney stones. Oranges are a healthful supply of fiber and have plenty of health advantages. Tangerines, a variation of oranges, are characterised by way of a higher liquid content material and decrease acidity and sugar content material. Their outer shell is normally reddish-orange in color. The peels, together with those of oranges and tangerines, are used to extract critical oils and make sweets. In addition, these peels include sugars, organic acids, and phenols, which offer them antioxidant homes and potential benefits towards bacteria and viruses [5-7]. It is really worth noting that ingesting or using the peels of end result and greens not simplest will increase fiber intake, however additionally reduces the quantity of meals thrown into the trash, which is a healthful and environmentally friendly practice [8]. The peels of some fruits inclusive of citrus culmination, even though sour in flavor, are characterized with the aid of high ranges of vitamins C, B2, B6, calcium, magnesium, potassium, and anti-inflammatory flavonoids, in order that they may be floor and utilized in salads [9]. Fiber and the nutrients they contain [10]. A study published in the International Journal of Molecular Sciences in 2012 showed that the outer shell of a fruit has a stronger antioxidant capacity than the inner core [11]. One of the main types of peels that are edible and have health benefits is the orange peel. One tablespoon of these peels (equivalent to 6 grams) contains 14% of the recommended daily intake of vitamin C, as well as provitamin A, folate and vitamin B2. Calcium, polyphenolic compounds, it is worth noting that about 90% of the essential oil in oranges is composed of limonene, which has anti-cancer and anti-inflammatory properties. Orange peels contain terpenes, which have anti-inflammatory properties and are also a good source of many other nutrients, such as: fiber and plant matter. It should be noted that these peels contain pesticide residues and may be difficult to digest due to their high fiber content and hardness. In addition, their texture and taste may be unpleasant to some people [12, 13]. The results of the study showed that there were differences in the content of heavy metals such as lead, cadmium, chromium and mercury in some fruits collected in Samawa city, Muthanna governorate, Iraq. According to the study [14], the concentrations found in the fruits were compared with the recommended limits to determine the level of food contamination. Although the range is slightly lower than the results of the study, it is consistent with the results of the study [15].

Applications such as the treatment of fruit plants with industrial wastewater. The use of pesticides and fertilizers increases the density of heavy metals in fruits containing chemicals such as "phosphates, heavy metals, non-biodegradable polychlorinated hydrocarbons; industrial wastewater and pesticides are the main causes of toxic heavy metal problems. Heavy metals can cause a variety of diseases such as gastrointestinal mucosal corrosion, cancer, coagulation disorders, vomiting blood, liver damage, blood in the stool, cardiotoxicity, nephrotoxicity, hepatotoxicity, immunotoxicity, shortness of breath, vomiting blood, black stools, heart disease, etc. Circulatory system problems, kidney and bone diseases, Alzheimer's disease, etc. Parkinson's disease is also associated with heavy metals. Heavy metals can also promote the formation of high levels of ROS, which are the main cause of cell damage, biomolecules and DNA. It is well known that most heavy metals have toxic effects on the body. However, some of them are important for normal growth and development of humans. In low concentrations, they are often called micronutrients. Therefore, the presence of chromium (Cr) in the blood can negatively affect insulin stability, which means that it reduces the body's ability to require insulin as a hormone. Cr also interacts with insulin in protein synthesis, and Cr deficiency affects glucose tolerance. Similarly, cobalt (Co) is needed to build hemoglobin and facilitate its function. Fats, carbohydrates, proteins, vitamins, hormones and enzymes have also confirmed that heavy metal concentrations exceed the levels recommended by the Food and Agriculture Organization of the United Nations/World Health Organization [16, 17]. This study aims to evaluate the potential contamination of various citrus samples collected from local markets in Anbar Governorate, Iraq, including oranges, tangerines, lemons, sandalwood and grapefruit. The focus is to determine the presence of heavy metals (iron, chromium, nickel, copper, cadmium and lead) and assess whether these elements are within acceptable safety levels based on international standards, thereby ensuring their suitability for human consumption. The purpose of this study is to examine the potential health benefits of citrus fruits, with a focus on lemons, oranges and tangerines. Brief Problem Statement: Although citrus fruits are rich in a variety of beneficial nutrients, there are significant differences in acidity between different types of citrus fruits. Some varieties, such as yellow lemons and green lemons, are very acidic and difficult to eat alone. On the other hand, oranges and tangerines are very sweet. The selection of appropriate citrus fruits must consider their hardness and weight in relation to their size. In addition, the peels of citrus fruits, including those of oranges and tangerines, have antioxidant properties and potential benefits against bacteria and viruses.

2. MATERIALS AND METHODS

Citrus samples were collected from local markets in Anbar Iraqi province (oranges, tangerines, lemons, sind, grapefruit), washed thoroughly with water, then peeled and separated the pulp. After ensuring that the sample is thoroughly dried, grind it into a fine powder with an electric blender and place it in a plastic container. To obtain a fine powder, you can also use a mortar and pestle instead of an electric blender. Digestion stage: After the sample is dried into a fine powder, weigh 2 g of each sample (pulp and peel) using a sensitive analytical balance, place each sample separately in a beaker and mix with 20 ml of concentrated hydrochloric acid. Acid and concentrated nitric acid 1:1 each. Analysis stage: The concentration of some heavy elements (iron, chromium, nickel, copper, cadmium and lead) is measured using a flame atomic absorption device.

The collected samples are taken to the laboratory and the concentration of heavy elements is measured there. For this purpose, flame atomic absorption spectroscopy (AAS) is used, which works by studying the wavelength of photons absorbed when the atoms of an element are excited. Each element has its own bulb, which represents a lamp unique to that element (hollow cathode lamp). The flame acts to convert the sample mist into atomic vapor because the atomic vapor absorbs the light emitted by the light source (hollow cathode lamp). All samples were examined for each element using this device [18], with the radiation source being a hollow cathode lamp.

A series of standard solutions were prepared from a high concentration standard solution (1000 ppm) of the prepared element salt, separated for each element. The required volume was first pipetted into a 500 mL volumetric flask and diluted to the required volume with distilled water. A series of standard solutions were then taken from the diluted standard solution using the dilution method [19].

$$C1V1 = C2V2$$

where,

C1 is the concentration of the first standard solution.
V1 is the volume of the first standard solution.
C2 is the concentration of the second standard solution.
V2 is the volume of the second standard solution.

Each element was estimated based on its wavelength. A standard solution of each element was prepared from a 1000 ppm stock solution, in addition to a chelate solution (blank) consisting of only the acid mixture.

Element estimation by flame atomic absorption spectrophotometer:

1. Determine the optimal operating conditions for the atomic absorption spectrophotometer.
2. The detection limit of the equipment and the type of flame used to estimate each measured element.
3. A series of standard solutions with a concentration of 1000 mg/l are prepared from the standard stock solution. This concentration range is below and above the concentration of the element to be estimated in the sample.
4. The pH value of the sample solution is acidic and ranges from 4 to 6.5, which affects the flow rate of the solution in the nebulizer. Therefore, the standard solution must be acidified by adding (4-5) drops of concentrated nitric acid.
5. Acetylene is used as a fuel.
6. After completing the above steps, we start the measurement process using an atomic absorption spectrophotometer [20].

The digested samples are recorded and checked accordingly. The measured absorbance is used to determine the metal concentration. The samples are analyzed repeatedly to ensure quality assurance and control. In order to obtain the average concentration used to prove accuracy, each sample must be analyzed multiple times. To evaluate precision, the standard deviation of the average is also calculated. The standard solution and the procedural blank are included in the analytical quality control procedure.

3. RESULTS AND DISCUSSION

The results showed that most of the observed concentrations of all minerals tested were below the maximum permitted concentrations of the FAO/WHO and, therefore, safe for human consumption. However, some citrus varieties collected from the markets of Anbar Province, Iraq, were found to have concentrations of certain minerals exceeding the permitted limits. All test results are listed in Table 1. Table 2 shows the statistical analysis results.

3.1 Iron (Fe)

As seen in Figure 1 and Table 1, iron contents varied from 1.10 in lemon pulp to 26.05 in grapefruit peel, and they did not go above the 425 FAO/WHO recommended levels [21]. Since iron is a component of hemoglobin, which aids in the transportation of oxygen to every part of the body, it is one of the advantageous and essential mineral components for human health. Furthermore, iron promotes the immune system, aids in the exchange of cholesterol, and helps the digestive system and body temperature to work. It also has an impact on the state of the nails, hair, and skin. However, since the body is unable to create this vital component on its own, nutrients continue to be the most significant source of it. Additionally, a person's age and gender determine how much iron their body needs each day. The body's muscles and tissues malfunction when iron levels are low, which can result in anemia. Malabsorption of iron, excessive blood loss, and malnutrition are some of the causes of anemia [22].

Table 1. Concentrations of heavy metals in studied citrus fruits

Elements (ppm) Citrus Fruits	Fe	Cr	Ni	Cu	Cd	Pb
Orange Pulp	16.63	428.1	ND	197.0	102.0	.2130
Orange Peels	78.2	570.1	046.0	141.0	097.0	ND
Tangerine Pulp	72.5	073.3	146.0	232.0	077.0	227.0
Tangerine Peels	10.64	198.1	162.0	217.0	097.0	618.0
Lemon Pulp	10.1	542.4	052.0	229.0	079.0	085.0
Lemon Peels	2.18	478.1	ND	041.0	048.0	.1500
Cindy Pulp	6.68	041.1	ND	222.0	097.0	.1820
Cindy Peels	8.97	ND	ND	057.0	084.0	618.0
Grapefruit Pulp	8.04	617.0	ND	134.0	098.0	.8120
Grapefruit Peels	26.05	ND	ND	136.0	099.0	0.094
FAO/WHO Limit	425	2.3	0.1	73	0.2	0.3
ND=Not Detected						

Table 2. The results of statistical analysis

Citrus Fruits	Orange Pulp	Orange Peels	Tangerine Pulp	Tangerine Peels	Lemon Pulp	Lemon Peels	Cindy Pulp	Cindy Peels	Grapefruit Pulp	Grapefruit Peels
Number of Values	5	5	6	6	5	5	4	5	5	4
Minimum	0.213	46	72.5	10.64	0.15	0.182	8.97	0.812	0.812	0.094
25% Percentile	8.422	62.1	73.1	75.41	1.165	3.431	20.98	4.426	4.426	6.583
Median	102	97	111.5	180.1	41	41.1	70.5	98	98	62.53
75% Percentile	312.6	355.6	228.3	317.3	263.1	159.5	484.5	375.5	375.5	126.8
Maximum	428.1	570.1	232	618	478.1	222	618	617	617	136
10% Percentile	0.213	46	72.5	10.64	0.15	0.182	8.97	0.812	0.812	0.094
90% Percentile	428.1	570.1	232	618	478.1	222	618	617	617	136
Mean	148.8	186.5	138	217.1	113.9	73.39	192	171.6	171.6	65.29
Std. Deviation	174.7	217.2	76.18	210.3	204.8	91.51	285.7	255.5	255.5	63.05
Std. Error of Mean	78.12	97.13	31.1	85.86	91.57	40.92	142.8	114.3	114.3	31.53
Lower 95% CI of Mean	-68.12	-83.23	58.02	-3.592	-140.4	-40.23	-262.6	-145.7	-145.7	-35.04
Upper 95% CI of Mean	365.7	456.1	217.9	437.8	368.1	187	646.6	488.8	488.8	165.6
Actual Confidence Level	93.75%	93.75%	96.88%	96.88%	93.75%	93.75%	87.50%	93.75%	93.75%	87.50%
Lower Confidence Limit	0.213	46	72.5	10.64	0.15	0.182	8.97	0.812	0.812	0.094
Upper Confidence Limit	428.1	570.1	232	618	478.1	222	618	617	617	136
Coefficient of Variation	117.41%	116.48%	55.22%	96.87%	179.80%	124.68%	148.81%	148.92%	148.92%	96.58%
Geometric Mean	31.39	122.9	121.1	128.2	12.52	16.08	71.78	35.05	35.05	13.47

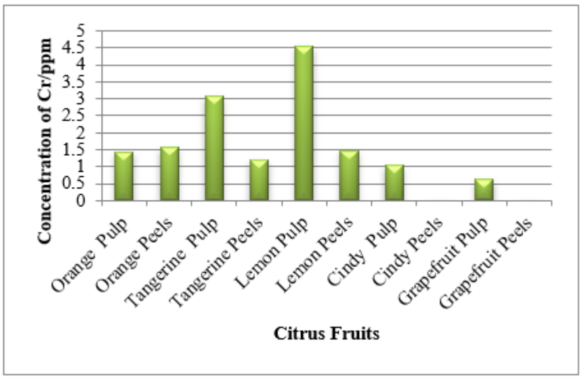

Figure 1. Iron concentrations in different types of citrus fruits

3.2 Chromium (Cr)

The results demonstrated that only two samples, orange pulp (3.073) and lemon pulp (4.542), had concentrations of chromium that exceeded the FAO/WHO's 2.3 standard [21], as demonstrated in Figure 2 and Table 1. Brief contact can lead to irritation of the skin and the development of ulcers. Over time, it can lead to kidney failure, liver damage, and tissue damage in the blood and nerves. Chromium is often stored in the aquatic organisms, this increases the probability of consuming fish that are exposed to high concentrations of chromium [22].

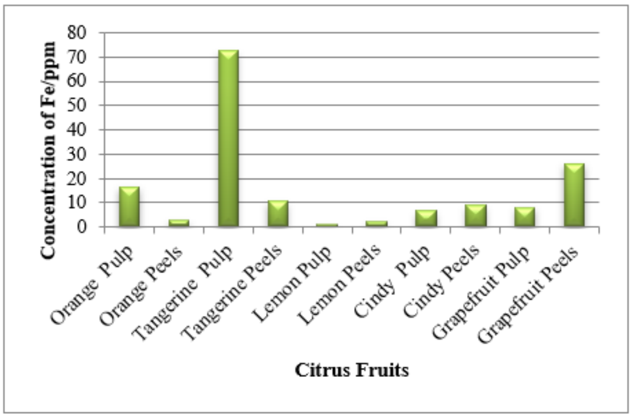

Figure 2. Chromium concentrations in different types of citrus fruits

3.3 Nickel (Ni)

As demonstrated in Figure 3 and Table 1, the FAO/WHO recommended value of 0.1 was only marginally exceeded in two samples, citrus seeds and citrus peels, with values of 0.146 and 0.162, respectively. Studies have demonstrated that the human body is capable of producing small quantities of nickel that result in the production of red blood cells, however, over a significant amount of this metal is toxic. Short-term overexposure to nickel does not cause health problems, but long-term exposure can cause weight loss, heart and liver damage, and skin irritation. The EPA (Environmental Protection Agency) lacks the authority to regulate the level of nickel in water intended for consumption. Nickel can be accumulated in aquatic animals, but its presence does not increase in magnitude as the chain of food succession proceeds [21, 22].

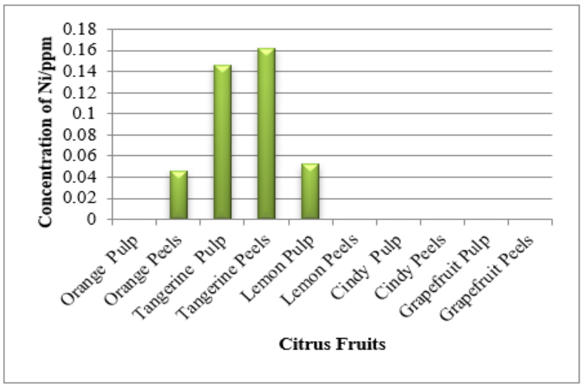

Figure 3. Nickel concentrations in different types of citrus fruits

3.4 Copper (Cu)

As can be seen in Figure 4 and Table 1, the concentration of copper in all of the tested samples was in the typical range of 73FAO/WHO [16], which was from 0.041 in the peel of lemon to 0.232 in the pulp of orange. Although copper is vital to human survival, too much of the metal can lead to anemia as well as damaging the liver, kidneys, stomach, and intestines. Increased copper consumption is associated with negative health effects in patients with Wilson's disease. Drinking water derived from copper pipes and chemicals intended to prevent algae growth typically contains copper [21, 22].

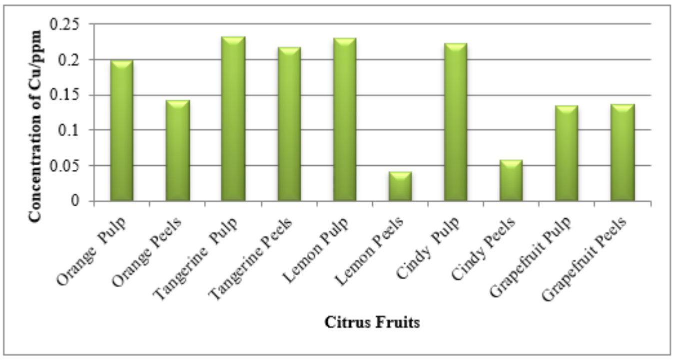

Figure 4. Copper concentrations in different types of citrus fruits

3.5 Cadmium (Cd)

As indicated in Figure 5 and Table 1, the cadmium concentration values did not surpass the standard norms of 0.2 FAO/WHO, ranging from 0.048 in lemon peels to 0.102 in orange pulp. Because of its resemblance to zinc and other vital micronutrients, cadmium has chemical toxicity characteristics. For humans, plants, and animals. The endurance of vigor is cadmium. Long-term exposure to obstructive pulmonary illness causes kidney failure, and it has been connected to lung cancer, though the data on this is hard to interpret because compound variables can also induce bone deformities (Lin).

Osteoporosis and bone health in both people and animals. Furthermore, despite the data collected contradicting these findings, the mineral has been connected to elevated blood pressure and its impact on the heart muscle in animals [19, 20].

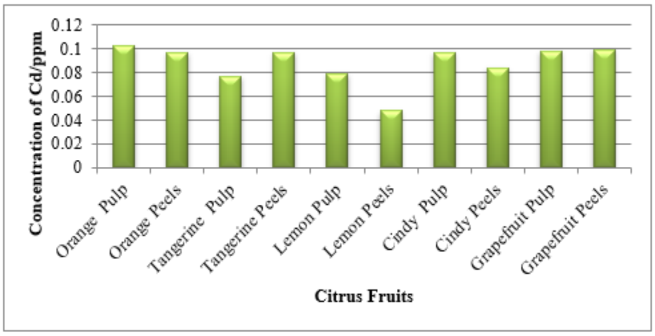

Figure 5. Cadmium concentrations in different types of citrus fruits

3.6 Lead (Pb)

The results showed that the lead levels in two different samples, namely, cinnamon peel (0.618) and grapefruit pulp (0.812), were well above the FAO/WHO's standard of 0.3, as can be seen in Figure 6 and Table 1. Studies have demonstrated that lead exposure can have a variety of biological consequences, depending on the magnitude and length of exposure. Different amounts have different effects, and children and adolescents are more susceptible than adults. High concentrations of exposure can lead to toxic chemical effects in the human body that are detrimental to the kidneys, heart, lungs, and skin. These effects can also lead to problems with the synthesis of hemoglobin, effects on the kidneys, digestive system, joints, and reproductive systems, and chronic or acute damage to the nervous system [21, 22].

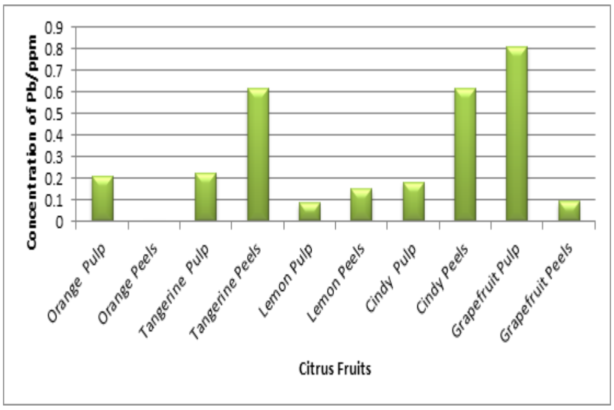

Figure 6. Lead concentrations in different types of citrus fruits

3.7 Public health relevance

Heavy metals such as lead, cadmium, and arsenic can Eventually, these metals are accumulated in the human body, and their consumption via food can lead to various health issues, including neurological disease, kidney failure, and cancer. Citrus fruits are commonly eaten because of their high content of vitamin C, anti-oxidants, and fiber, they also have a significant role in human consumption. However, if these fruits have high concentrations of heavy metals, they may unwittingly contribute to the body's metal pollution. By measuring the heavy metal concentrations in the pulp (the edible part) and the peel of citrus fruits, this research provides information that is valuable in regards to the potential health dangers associated with the consumption of these fruits [23, 24].

3.8 Environmental safety relevance

Agricultural practices, soil quality, and irrigation water can influence heavy metal accumulation in citrus fruits. If contaminated water or soil is used for cultivation, it may lead to elevated heavy metal levels in the fruits. The study's findings can inform agricultural practices and food safety guidelines. For instance, monitoring water quality: Ensuring that irrigation water is free from heavy metals is essential to prevent contamination of citrus fruits.

Proper waste disposal: Proper disposal of citrus peels (which may contain higher metal concentrations) can prevent environmental pollution [25, 26].

3.9 Consumer awareness

Educating consumers about the potential dangers of heavy metal accumulation in citrus fruit can help to promote healthy consumption behavior.

Overall, this research helps to elucidate the degree to which heavy metals are polluting citrus fruit and highlights the necessity of public health awareness and environmentally responsible behavior in the production and consumption of fruit.

4. CONCLUSIONS

1. Safety of human consumption:

The concentrations of heavy metals in the majority of citrus fruits were below the accepted limits of international regulations.

The concentrations of toxic metals like cadmium, lead, nickel and chromium were typically low or below the detection threshold, especially in citrus fruit juices.

The peel of citrus fruits had the second lowest concentration of metal, this indicated that the fruit had the least amount of metal accumulation.

2. Differential accumulation:

The accumulation of metals is different for different plant species, tree segments and fruit.

Essential nutrients like iron, manganese and zinc are primarily located in leaves and stems.

3. Factors that affect the accumulation:

The quality of the water used for irrigation, the soil's pH and the transfer factors from soil to plant affect the capacity to absorb metals with a heavy burden.

Other considerations include temperature, humidity, the availability of organic material and other nutrients.

4. Take care when dealing with polluted water:

The primary treated wastewater should not be utilized to irrigate plants that are edible due to the potential for heavy metal generation.

5. STUDY LIMITATIONS

Sample size: The investigation may have a deficiency of citrus fruit samples that can be analyzed. A larger sample size would increase the statistical significance of the results.

Sample variability: Heavy metal concentrations in citrus fruit may differ between batches or seasons, which would affect the validity of the results.

Accuracy: The measurement of analytes using atomic absorption spectrometry (AAS) may have a slight error. Maintaining the consistency and fidelity of the AAS method is essential.

Variation: Heavy steel degrees in citrus fruit can also vary depending on the location, soil type, and other environmental elements. These variations need to be considered.

Single analytical technique: Abstaining entirely on atomic absorption spectrometry may also impede the comprehensive assessment of heavy metals. Combining AAS with different strategies, consisting of ICP-MS, can cause a greater comprehensive understanding.

6. FUTURE PROSPECTS

Biofortification: Investigate strategies to enhance the accumulation of crucial nutrients (e.g., zinc, selenium) in citrus result even as minimizing toxic heavy metals.

Phytoremediation Enhancement: Explore ways to improve the herbal capacity of citrus plants to soak up and sequester heavy metals from infected soils.

Molecular Mechanisms: Study the genetic and molecular mechanisms underlying heavy metal uptake, delivery, and detoxification in citrus vegetation.

Health Risk Assessment: Conduct epidemiological studies to evaluate the fitness dangers related to long-time period intake of heavy metal-contaminated citrus culmination.

Sustainable Cultivation Practices: Develop hints for secure citrus cultivation, thinking about soil management, irrigation, and fertilization practices.

Public Awareness: Educate customers about heavy metal risks and safe fruit consumption practices.

In summary, addressing those limitations and exploring new avenues will make a contribution to advancing our information of heavy steel concentrations in citrus end result and their implications for human health and environmental protection.

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