

Review Article

Comparisons of Different Digestion Methods for Heavy Metal Analysis from Fruits

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Abstract

Fruit juices are produced in home or industrially from horticultural crops by pressing the liquid part. They are rich in sugar, vitamins, and minerals like iron, copper, potassium, folate minerals, and vitamins A, B, and C which are essential for giving the body the nutrients it needs to stay healthy since fruits contain vital mineral components like copper (Cu), iron (Fe), and manganese (Mn), which is necessary for human growth and respiration. However, they may have heavy metals which may poison health risk and toxic even the presence is in little amount. Since fruit juices doesn't pass through different processes, except extracting the liquid from the fruits of vegetables contamination and heavy metals affect human health. Before determination of heavy metals different procedures are applied for analysis. Digestion is the key component for determination of heavy metals from different samples. In this paper we are concerned on wet digestion methods for analysis. Closed system wet digestion is preferred since it lower the risk of contamination. There are different wet digestion types. Some of them are conventional wet digestion, ultraviolet digestion, ultrasound-assisted acid decomposition, conventional heating, microwave-assisted wet digestion etc. From thus, microwave digestion procedure was preferred for the digestion of samples for determination of heavy metals due to its ability to oxidize almost all of the organic samples.

Keywords

Contamination, Decomposition, Digestion, Fruit Juices, Heavy Metals, Minerals, Wet Digestion

1. Introduction

Fruits are horticulture crops that are typically consumed unprocessed, however occasionally they may be prepared in a home or industrial setting. Fruit Juices are the processed fruit that are used in homes and businesses [1]. Fruit juices are made by pressing the liquid out of one or more fruits. They provide our bodies with readily absorbed fruit sugar, vitamins, and minerals like iron, copper, potassium, folate minerals, and vitamins A, B, and C. Regular fruit eating is essential for giving the body the nutrients it needs to stay healthy since fruits contain vital mineral components like copper (Cu), iron

(Fe), and manganese (Mn), which are necessary for human growth and respiration [2].

It's possible that these fruit juices may include hazardous metals that are very bad for people's health. Because heavy metals like lead (Pb), nickel (Ni), arsenic (As), chromium (Cr), and palladium (Pd) can be hazardous to humans even at low concentrations, the accumulation of these metals in food can be harmful to all individuals. Vegetables and fruits may become contaminated with toxic heavy metals from different sources [2]. Although heavy metals are naturally present in

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the earth, human activity causes them to concentrate. Common sources include lead-acid batteries, car emissions, treated wood, paints, fertilizers, and industrial and mining wastes. The most common heavy metal contamination is lead. It was widely utilized as a constituent of tetra-ethyl lead in gasoline [3].

Most of these heavy metals, such as Cd, Ni, and Cr, are carcinogenic. They also present a number of health risks to people, including the possibility of poisoning from contaminated drinking water and the development of chronic diseases due to their accumulation in the body [4]. According to International Agency for Research study, cancer may cause by cadmium intake. The interaction of the metal with biological electron-donor groups, including sulfhydryl groups, causes lead and cadmium poisoning by interfering with a variety of enzymatic functions. Symptoms related to the hematological, peripheral, renal, gastrointestinal, and central neurological systems are among the clinical signs of lead intoxication. The body absorbs cadmium, a cumulative nephrotoxicant, through food and cigarette smoking [5].

Eating vegetables has been linked to dietary exposure to heavy metals, specifically Cd, Pb, Zn, and Cu, which poses a risk to human health. Higher amounts might be hazardous to the biota, disrupt the metabolic process, and result in other problems [6].

Table 1. WHO/FAO Acceptable Limit of heavy metal levels in the fruits juices (mg/kg).

Heavy Metals	WHO/FAO Acceptable Limit (mg/kg)
Cadmium (Cd)	0.10
Copper (Cu)	0.05 – 0.5
Zinc (Zn)	99.40
Iron (Fe)	0.80
Lead (Pb)	0.20 (0.1 for orange)
Nickel (Ni)	0.14
Manganese (Mn)	0.30
Cobalt (Co)	2.00

Source: [7]

2. Digestion of Heavy Metals

Digestion is decomposition of metals for analysis. It is essential part of laboratory process. Wet digestion and dry ashing are the two types of decomposition methods that are frequently used to determine the presence of trace elements in biological and environmental materials [8]. The most analytical techniques are more frequently used with the wet digestion procedure. This kind of decomposition process is used

since there is less risk of losses at the lower working temperature [9]. In order to reduce or eliminate analyte loss while using the dry ashing method, ashing aids and careful temperature control are necessary. The main cause of contamination in this breakdown process is the employment of several chemicals, both as ashing aids and for the sample ash dissolving. Likewise, an even greater source of contamination arises from the wet digesting procedures' use of comparatively larger volumes of chemicals. Other methods based on closed systems were developed as a result of worries about the contamination and element loss issues associated with both types of decomposition methods. These methods include direct dissolution with tetra alkylammonium hydroxide, wet decomposition in pressure bombs, combustion in oxygen flasks, and oxygen bombs and other combustion systems [10].

Wet Digestion

Using concentrated acids or their combinations, wet digestion is used to oxidize the organic portion of materials or remove elements from inorganic matrices [11]. It is typically done in closed systems at high pressure (digestion bombs) or in open vessels (tubes, beakers, hot plates, heating blocks) using a variety of energy sources, including thermal, ultrasonic, and radiant (infrared, ultraviolet, and microwave). Compared to dry ashing, wet digestion provides significantly more possibilities in terms of reagent and equipment selection. However, the nature and composition of the sample as well as the concentration and composition of the reactive mixture should be considered prior to analysis [12].

It comprises the following: the reagent's safety and purity; the acid's strength; its boiling point and oxidizing power; and the solubility of the resultant salts. According to (Szymczycha-Madeja and Mulak (2009), HNO_3 , HCl , H_2SO_4 , H_3PO_4 , HClO_4 , HF , and H_2O_2 are typically utilized for organic materials, alloys, minerals, soils, rocks, and silicates [13]. For three reasons, wet digestion in closed operations was chosen over dry ashing. It produced more accurate results, took less time, and improved sample recovery [12]. Furthermore, this method is better suited for determining Cu, Mn, Fe, Zn, Se, and Al in different dietary samples due to the derived analytical parameters [14].

Materials and Reagents

One technique for breaking down matrix components into their most basic chemical forms is sample wet digestion. Energy sources like heat, chemical reagents like acids, or a mix of the two are used to create this digestion. When a reagent is utilized, its type will be determined by the matrix [12]. The sample size, which in turn depends on how sensitive the determination method is, determines how much reagent is utilized [15]. However, since there are numerous potential sources of inaccuracy, such as partial digestion of the analytes present or contamination from the chemical vessels, the procedure of placing a material into solution is frequently the most crucial stage of the analytical process [16].

Most common materials for digestion are:-

Borosilicate glass (SiO_2):- 800 °C is the operating temper-

ature. It is unfavorable for use in processes involving wet digestion.

Poly tetra fluoro ethylene (PTFE):- The operating temperature is $< 250^{\circ}\text{C}$. In pressure decomposition systems, it usually has restrictions to use with decomposition vessels.

Fused quartz (SiO_2):- The operating temperature is $< 1200^{\circ}\text{C}$. Quartz is the best material for vessels in all processes involving the moist digestion of organic material.

Graphite (Glassy carbon):- With $< 500^{\circ}\text{C}$ operating temperature. Glassy carbon is utilized as crucibles, pans, and receptacles for wet digesting processes and alkaline melts.

Most wet digesting techniques employ a combination of hydrogen peroxide, oxidizing acids (HNO_3 , hot concentrated HClO_4 , hot concentrated H_2SO_4), and non-oxidizing acids (HCl , HF , H_3PO_4 , diluted H_2SO_4 , diluted HClO_4). All of these acids are corrosive by nature especially when heated and concentrated, care should be taken when handling them to prevent accidents and injuries [17]. Commercially available concentrated acids that meet the necessary high purity standards can be further refined using sub boiling distillation [18].

The term "decomposition" describes a more complex process that usually involves the use of chemicals and specialized equipment and is done at greater pressure and/or temperature levels. [19]. Acid-treating samples are a common procedure in many laboratories to separate pertinent elements from the sample matrix and transfer them to a liquid matrix for additional analysis. Dissolution is the popular term for the simple process of dissolving a material in a suitable liquid at a relatively low temperature, either with or without a chemical reaction. Usually wet digestion is the most conventional and extensively used technique for digesting both organic and inorganic samples [12].

Open System Wet Digestion

The classical method of wet digestion is carried out in open vessels. Its limited temperature range at normal pressure stems from the low boiling temperatures of key reagents, including hydrogen peroxide, hydrochloric acid, and nitric acid. As a result, the digestion efficiency of this method is typically low, and the possibility of systematic errors is relatively high. One of the first methods and unquestionably the most used one for sample disintegration or dissolving of organic and inorganic sample materials in chemical laboratories is open vessel acid digestion. Due to its ease of automation and easy control over all important parameters (time, temperature, and addition of digesting reagents), this incredibly cheap procedure has enormous utility for routine analysis [9].

There are different distinct procedures as well as slight modifications to existing approaches. Wet digestion's primary benefit over dry ashing is its quickness. These systems are constrained, however, in that their maximum digestion temperature is low and cannot rise over the matching acid or acid mixture's boiling point at ambient pressure [20]. For example, at such low temperatures (boiling point 122°C), the oxidizing power of nitric acid with respect to many matrices is insufficient [12]. Sulfuric acid is one potential cure; it raises the

temperature of a digesting solution considerably [21]. The matrix and the determination procedure determine whether or not this expedient is practical. At atmospheric pressure, samples with high fat and protein content typically do not undergo complete digestion. The possibility of contamination through laboratory air, the need for relatively large amounts of reagents (which frequently involve expensive reagents), and the risk of losing trace components are further drawbacks [22]. Reflux condenser use in conjunction with an excess of acid (mostly nitric) and temperature and duration adjustment might minimize losses. However, in terms of worker safety, atmospheric pressure devices are the preferable option [23].

Conventional wet digestion

Conventional method of wet decomposition involves a system that has a heated conventional source (heating plate, sand bath, Bunsen burner, etc.) that can operate according to a temperature program or at a set temperature. Many times, acid breakdowns are carried out in any type of vessel, most commonly a glass or PTFE beaker, conical flask, etc., with or without a refluxing condenser [22]. Refluxing, however, is required when a material breaks down in an open wet digesting process [9].

Digestion agents that are frequently used include hydrogen peroxide, nitric acid, sulfuric acid, hydrofluoric acid, perchloric acid, and various mixtures of these [24]. Aqueous or organic matrices, including surface waters, waste water, biological and clinical samples, food samples, soil, sediment, and sewage sludge, coal, high-purity materials, and different technological materials, are used in the majority of wet decomposition applications. Open systems have developed more recently, and decomposition ramps often consist of many containers with reflux condensers to prevent the reactive mixture from evaporating and to decrease the potential volatilization loss of some analytes. For the purpose of guaranteeing the simultaneous digestion of a large series of samples, such an assembly is perfect [22].

Microwaves are the most inventive energy source for wet decomposition processes. Microwave decomposition is more efficient than traditional heating because the heating occurs inside the decomposition mixture [25]. Microwaves are frequently used to increase the rate and effectiveness of breakdown for specific types of materials that are thought to be challenging to solubilize. Additionally, some instrumentation makes automation conceivable [26, 27].

Ultraviolet digestion

Since UV-digestion doesn't need for the addition of a lot of chemicals, it is a clean sample preparation technique [28]. Organic molecules in samples have been broken down and turned into minerals using the UV-photolysis digesting process [29]. UV radiation is seen to be an environmentally benign and efficient method of destroying organic debris, as well as a way to reduce the possibility of contamination or sample loss due to evaporation. UV radiation (light) breaks down liquids or slurries of solids in the presence of trace amounts of hydrogen peroxide, acids (mostly HNO_3), (i.e.,

drinks, specific industrial waste water, sewage treatment plant water, soil extracts). Free metal ions are produced by the breakdown of complexes of the analyte elements and dissolved organic matter (DOM).

To ensure a high photon flux, the matching digestion vessel should be placed close as feasible to the UV lamp (low or high pressure) [30]. The production of OH[•] radicals from water and hydrogen peroxide during photolysis, which is initiated by UV radiation, is a characteristic of the digestive process [31]. These reactive radicals have the ability to oxidize organic materials found in simple matrices containing up to 100 mg/l of carbon to carbon dioxide and water. Of course, the only ways to completely eliminate the matrix are either with simple matrices or by combining photolysis with other digestive methods [22].

Ultrasound-assisted acid decomposition

While pretreating solid samples, ultrasound is helpful since it speeds up and simplifies processes like fusion, decomposition, and dissolution, among others. It has been possible to decompose acid using an ultrasonic device (a probe or bath) [32]. Via compression and rarefaction, ultrasonic waves with a minimum frequency of 16 kHz propagate, causing a large number of microscopic cavities to form, the generation of free radicals, the dispersal of chemical layers, and an acceleration of the reaction's ingredient contact [33]. Because emulsification is encouraged and mass heat transfer in two-phase systems is amplified, ultrasonic effects are typically far stronger in heterogeneous chemical systems than in homogeneous ones [34]. These effects have been used in biological, environmental, and agricultural chemistry to prepare samples [35].

Closed system Wet Digestion

For trace and ultra-trace analyses, closed system digestion is highly useful, especially in situations where sample supply is constrained. An arbitrary difference between low (simple) pressure digestion and high-pressure digestion should be formed since the oxidizing power of a digestion reagent has a considerable reliance on temperature. The maximum temperature for low-pressure digestions (less than 20bar) is approximately 180 °C, whereas high-pressure digestions (more than 70bar) can reach temperatures above 300 °C [22].

They have been effectively utilized for the digestion of a range of materials and are currently being employed to increase oxidation efficiency and shorten digestion times [36]. High pressures above atmospheric pressure can be employed in closed systems. This enables boiling at greater temperatures and frequently results in the majority of samples dissolving completely.

The absence of element volatilization, lower reagent quantities, and lack of contamination from outside sources are the benefits of a closed system over an open one. Using the closed digestion technique, the material is put into a vial (or bomb), which is typically made of a fluorinated polymer like perfluoroalkoxy (PFA) or poly tetra fluoro ethylene (PTFE) [12]. The bomb is sealed tightly and put in the microwave oven to be irradiated with

microwave energy once the digesting reagents have been added [22]. While conventional heating can also be used for digestion in closed vessels, microwave radiation has been used in the majority of recent applications due to its short turnaround time and ability to accommodate specific uses requiring the removal of matrix and high purity reagents.

Conventional heating (thermally convective wet pressure digestion)

Because convectively heated pressure vessel systems produce elevated digestion temperatures (approximately 200–230 °C), they have shown to be the most valuable methods for ensuring complete, or almost total, digestion of solid materials. Although glassy carbon or quartz vessels with PTFE holders are available for trace analysis, the majority of sample vessels used in thermally convective pressure digestion are made of PVDF, PFA, or PTFE. After mounting the sample vessel in a stainless steel pressure autoclave, it is heated to the appropriate temperature, commonly in a furnace, heating block, or drying oven used in laboratory settings [22]. Mechanized multi sample pressure digestion systems capable of processing relatively large sample numbers of the same matrix type were created in response to the need to evaluate many samples [12]. To enable quick manipulation of the solution created right away after withdrawing the "digestion bomb" from the oven or heating block, a cooling circuit can be installed into the metal case (jacket). Mixing the reactants can also speed up dissolution; however, use a stirring bar (coated in PTFE) is preferred. The Teflon digestion double vessel is filled with a tiny screw-cap vial for sample digestion. A Teflon-lined membrane pressure meter and thermocouple were used in the construction of a system to enhance the handling of pressure-temperature assessment and the carbon balance for specific materials. A unique design for a digesting tank meant to be used with a convection oven was recently developed. It is composed of three nested structures: an outside stainless steel shell, an intermediate 100 mL capacity PTFE container, and an inner 30 mL capacity PTFE container [22, 37].

Microwave heating (microwave-assisted pressurized wet digestion)

Temperatures above 300 °C can be used depending on the vessel material. Pressurized wet digestion in closed vessels, sometimes known as "digestion bombs," allows the digestion at greater temperatures, enhancing digestion efficiency (increased oxidation capability and improved dissolving rate).

The ability to oxidize almost all of the organic sample's contents using only pure nitric acid and produce digests with the lowest possible residual carbon content (RCC) is a crucial feature. Closed systems can also significantly lower the hazards of contamination, analyte losses, and reagent use. The high rise in the decomposition rate, which yields a high sample throughput in a short amount of time, is the driving force behind the development of microwave (MW)-assisted sample digestion techniques. A quick and even heating is facilitated by the phenomena of dipole rotation and ionic migration brought on by MW radiation inside the solution [38].

Microwave technology improves chemistry in sample

preparation by enabling faster reaction times, fewer discrete sample preparation processes, and higher sample homogeneity following digestion, higher sample throughput, and improved precision. Additionally, throughout method development, the procedures are ideal for standardization and automation. But at high temperatures, high pressure, and acid vapor present security risks [39].

3. Conclusion

Generally with the use of a reflux condenser, there is a substantial danger of analyte loss when samples are dissolved in an open vessel. Microwave-assisted wet digestion and, in particular, microwave-assisted pressurized on-line digestion seems to score highly in terms of economic features (low procurement, quick digestion time, high sample throughput). The digesting process indicates that the only ways to completely degrade many samples are either to use a closed wet digestion system in conjunction with UV irradiation, or to use a Teflon- or quartz-lined pressure vessel at high pressure and high temperature [22].

From wet digestion methods micro wave digestion method is better than others. It is due to microwave digestion procedures in the samples provided a simpler, effective, faster, less contamination, increases analytes recoveries and useful for volatile elements than dry and wet digestion methods in terms of digestion efficiency and recoveries analytes.

Conflicts of Interest

The author declares no conflicts of interest.

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