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Qurina Scientific Journal
ISSN: 2959 - 7463

Comparison of dry and wet digestion procedure for determination of heavy metals contents in vegetables

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Abstract: This study aims to compare two sample preparation methods, dry-ashing digestion and wet digestion, for determining the concentrations of lead (Pb), chromium (Cr), zinc (Zn), manganese (Mn), and copper (Cu) in eight different vegetable samples. Atomic absorption spectroscopy (AAS) was utilized to measure the heavy metal concentrations after sample preparation using the two methods. The findings indicated that the dry-ashing method yielded higher concentrations for lead, chromium, and zinc, while the wet digestion method was more effective for manganese and copper. The relative standard deviation (RSD%) values for both methods were comparable, ranging from 0.98% to 2.92%.

Keywords: dry-ashing, wet digestion, vegetable, heavy metal, AAS.

Introduction

The effects of heavy metals are important in daily nutrition due to their essential nutritional value on the one hand and their potential harmful effects on the other. Metals such as iron, copper, zinc, cobalt, and manganese are essential minerals because they play important roles in biological systems, but they can have harmful effects when consumed in excess of the recommended amounts. Meanwhile, elements such as mercury, lead, and cadmium have no nutritional significance and can be toxic even in small amounts [1].

On the other hand, vegetables are a good source of many essential minerals for the human body. In addition to elements such as magnesium, sodium, potassium, iron, and zinc, vegetables contain small amounts of copper, manganese, selenium, and others. Therefore, the presence of vegetables in the human diet is very important for maintaining health [2].

Many methods are used to estimate heavy metal concentrations, including atomic absorption spectrometry, which requires sample decomposition. Therefore, the procedures for extracting metals are of great importance to obtain the desired analytical results. The key to success in heavy metal analysis is to choose the appropriate sample preparation method that can provide accurate information about metal concentrations in samples. Therefore, several points should be taken into account when preparing samples, including: the type and amount of the sample, the composition of the sample, the quantities of elements, the need for total or partial digestion, and the instruments used for analysis [3].

Atomic absorption spectrometry (AAS) is the most widely used and recommended technique for the determination of heavy metal and metal contaminant concentrations due to its sensitivity, ease of use, accuracy, and specificity. Flame and graphite furnace are the two main techniques used in food analysis laboratories to determine metal concentrations in analyzed samples [4].

Wet and dry ashing is one of the most commonly used methods for sample decomposition and preparation prior to heavy metal determination. Each method has its own advantages and disadvantages [5].

Many studies have been conducted to compare the results of residual metal analysis after sample preparation using different sample digestion methods. One such study was conducted by researchers from Turkey on a set of spices collected from the Turkish market from different cities. The recovery values for copper, cadmium, lead, and iron were between 95-98% for the wet digestion method and between 95-96% for the dry digestion method. At the same time, the relative standard deviation (RSD) values were less than 10% in all samples [6].

This study aims to investigate the differences between two sample preparation methods (wet digestion and dry digestion) by estimating the concentrations of some metals in a set of vegetables collected from the local market in Tobruk, Libya. The goal is to determine which method (currently used in Libyan laboratories) is the best for determining the concentration of metals in plant samples.

MATERIALS AND METHODS

Samples of the edible vegetables that were imported from Egypt collected from Tobruk Central Vegetable Market in April 2023, the samples were randomly collected.

The vegetables were first washed in fresh running water to remove any dirt, dust, or parasites. They were then washed with distilled water to remove any remaining contaminants. The vegetables were then sliced and dried in an oven at 90 degrees Celsius for 48 hours. After drying, the vegetables were ground into a fine powder [7].

For dry-ashing digestion method processes according to AOAC [8], two grams of dry matter for each sample was weighed in a porcelain crucible and burn it on hot-plate at 120°C. After burning, ash was obtained at 550°C in a muffle furnace for four hours. Then the ash was dissolved with 5ml 1N Nitric Acid and after 2 hours the solution transferred to a 100-ml calibrated flask and filtered with filter paper and fill to 100 ml with same diluted acid. A blank sample was prepared concurrently with the experimental samples, employing the identical protocol.

For wet digestion method processes according to Sneddon [9] by “Modified Aqua Regia”, two grams of each individual sample were precisely weighed and transferred to designated Kjeldahl flasks. Subsequently, 20 milliliters (mL) of concentrated nitric acid with a 70% concentration were carefully added to each flask, followed by the controlled addition of 10 mL of hydrogen peroxide. The prepared samples were then allowed to undergo digestion for a period of 24 hours.

Subsequently, the samples were subjected to thermal treatment on an electric heating apparatus, maintaining a temperature range between 120-150°C. This process continued for approximately 30 minutes until the volume of each sample within their respective Erlenmeyer flasks was reduced to roughly 5 milliliters. Following the heating process, the samples were allowed to cool to ambient temperature. Subsequently, 30 milliliters of deionized water were added to each sample, followed by vigorous agitation to ensure complete extraction of residual solutes from the boiling vessel. Each sample was then subjected to filtration through a

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ISSN: 2959 - 7463

quantitative filter paper into pre-weighed 100-milliliter volumetric flasks. The beakers were subsequently rinsed with additional deionized water to quantitatively transfer any remaining sample material to the volumetric flasks. These flasks were then filled to the volumetric marking with deionized water, ensuring a final volume of 100 milliliters. A blank sample was prepared concurrently with the experimental samples, employing the identical protocol.

Concentrations of heavy metals (Pb, Cr, Zn, Mn, and Cu) were measured by Drawell DW-AA320N Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

The average concentrations of Pb, Cr, Zn, Mn, and Cu in eight product samples, prepared using two different methods, are presented in Tables 1 and 2 (Concentration mg/L).

Table 1: Concentrations of heavy metals in samples prepared by wet digestion

	Pb	Cr	Zn	Mn	Cu
1	0.676	0.0563	0.199	0.738	0.022
2	0.591	0.0306	1.097	0.433	0.176
3	0.476	0.0174	2.24	0.323	N D
4	0.638	0.0468	0.148	0.941	0.37
5	0.757	0.5124	1.744	1.249	2.609
6	0.867	0.1725	1.98	1.371	0.56
7	0.72	0.0223	N D	0.664	0.196
8	0.015	0.0233	N D	0.621	0.517

Table 2: Concentrations of heavy metals in samples prepared by dry-ashing digestion

	Pb	Cr	Zn	Mn	Cu
1	0.834	0.151	2.451	0.535	N D
2	0.792	0.089	3.065	0.278	N D
3	0.441	0.125	4.247	0.288	N D
4	0.662	0.5639	1.763	1.018	0.012
5	1.146	1.52	3.343	1.151	2.81
6	1.053	0.418	5.011	1.282	0.902
7	0.5	0.102	2.626	0.494	N D
8	0.432	1.916	2.501	0.479	N D

The comparison of lead content in samples after digestion by the two methods is shown in Table 3. There is a significant difference in the readings obtained using the dry digestion method compared to those obtained using the wet digestion method. The concentration readings for all samples, except sample 3, were higher when prepared using the dry method compared to the wet method. Additionally, the %RSD values were all below 2.37%.

Table 3: Comparison of Lead Content in Samples After Digestion by the Two Methods

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Preparation method		Wet digestion		Dry digestion	
Clues		mg/L	%RSD	mg/L	%RSD
Samples	1	0.676	2.27	0.834	2.1
	2	0.591	1.52	0.792	1.78
	3	0.476	2.15	0.441	2.2
	4	0.638	1.5	0.662	1.12
	5	0.757	2.37	1.146	1.88
	6	0.867	2.2	1.053	2.2
	7	0.72	1.98	0.5	2.2
	8	0.015	2.9	0.432	1.19

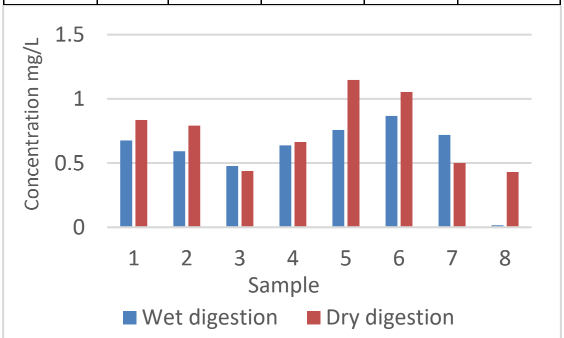

Figure 1: Comparison of Lead Concentrations in Samples Prepared by the Two Methods.

The comparison of chromium content in the samples is presented in Table 4. The results were consistent with those for lead. The concentration readings in all samples prepared using the dry method were significantly better than those prepared using the wet method. Additionally, the percentage relative standard deviation (%RSD) for all samples was below 2.72%.

Table 4: Comparison of chromium Content in Samples After Digestion by the Two Methods

Preparation method		Wet digestion		Dry digestion	
Clues		mg/L	%RSD	mg/L	%RSD
Samples	1	0.056	1.21	0.151	1.92
	2	0.031	1.73	0.089	1.6
	3	0.017	2.34	0.125	2.41
	4	0.047	2.69	0.564	3.01
	5	0.512	1.98	1.52	0.99
	6	0.172	2.11	0.418	1.13
	7	0.022	1.1	0.102	1.85
	8	0.023	2.72	1.916	1.51

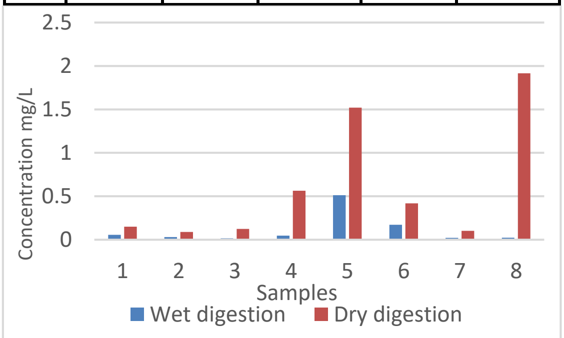

Figure 2: Comparison of chrome Concentrations in Samples Prepared by the Two Methods.

The comparison of zinc content in the samples is presented in Table 5. The results indicate a significant difference in readings, favouring the samples prepared by dry-ashing. Notably, samples 7 and 8, which were prepared by wet digestion, did not show any detectable values. Additionally, the %RSD values for all samples were below 2.92%.

Table 5: Comparison of Zinc Content in Samples After Digestion by the Two Methods

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Qurina Scientific Journal
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Preparation method		Wet digestion		Dry digestion	
Clues		mg/L	%RSD	mg/L	%RSD
Samples	1	0.199	2.33	2.451	2.92
	2	1.097	2.51	3.065	1.1
	3	2.24	1.16	4.247	1.16
	4	0.148	1.92	1.763	2.35
	5	1.744	2.58	3.343	1.87
	6	1.98	2.1	5.011	1.01
	7	N D	-	2.626	2.14
	8	N D	-	2.501	1.92

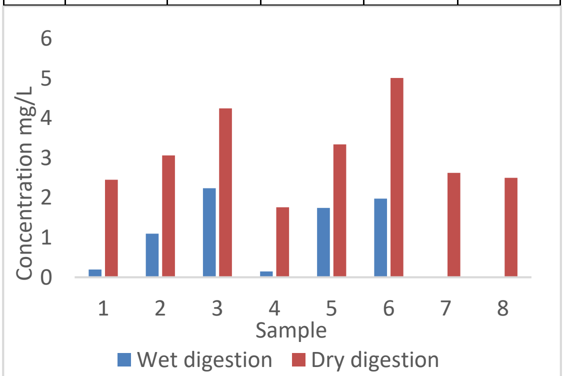

Figure 3: Comparison of Zinc Concentrations in Samples Prepared by the Two Methods.

The manganese readings differed from those of the previous metal. Except for sample 4, the samples prepared by wet digestion showed higher readings compared to those prepared by dry digestion, as shown in Table 6. Additionally, the %RSD values were all below 2.9%.

Table 6: Comparison of Manganese Content in Samples After Digestion by the Two Methods

Preparation method		Wet digestion		Dry digestion	
Clues		mg/L	%RSD	mg/L	%RSD
Sampl	1	0.056	1.21	0.151	1.92
	2	0.031	1.73	0.089	1.6
	3	0.017	2.34	0.125	2.41
	4	0.047	2.69	0.564	3.01
	5	0.512	1.98	1.52	0.99
	6	0.172	2.11	0.418	1.13
	7	0.022	1.1	0.102	1.85
	8	0.023	2.72	1.916	1.51

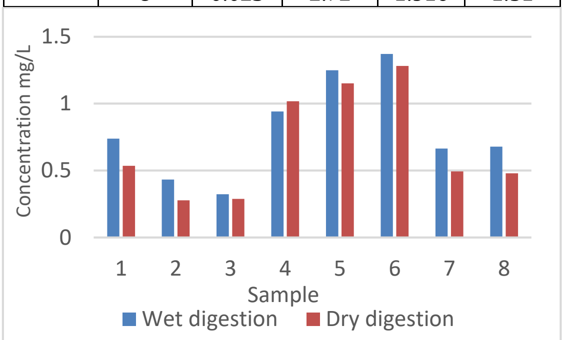

Figure 4: Comparison of Manganese Concentrations in Samples Prepared by the Two Methods.

The copper concentration readings differed significantly from the previous results. The samples prepared using wet digestion yielded much higher readings compared to those prepared by dry digestion. Specifically, in five out of eight samples prepared by dry digestion, no copper readings were obtained, as detailed in Table 7.

Preparation method		Wet digestion		Dry digestion	
Clues		mg/L	%RSD	mg/L	%RSD
Samples	1	0.022	1.19	N D	-
	2	0.176	1.82	N D	-
	3	N D	-	N D	-
	4	0.37	2.64	0.012	1.23
	5	2.609	2.01	2.81	2.2
	6	0.56	1.66	0.902	2.91
	7	0.196	2.01	N D	-
	8	0.517	2.1	N D	-

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ISSN: 2959 - 7463

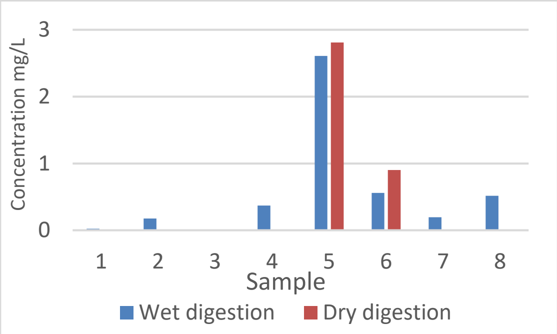

Figure 5: Comparison of Cupper Concentrations in Samples Prepared by the Two Methods.

Conclusion

The results highlighted significant differences between the two methods:

- **Lead and Chromium**: The dry-ashing method produced higher concentrations of lead and chromium in the samples compared to the wet digestion method. This suggests that dry-ashing may be more effective for detecting these metals.
- **Zinc**: Zinc concentrations were significantly higher in samples prepared by dry-ashing. In some cases, wet digestion failed to detect zinc altogether, indicating the superior efficacy of dry-ashing for zinc analysis.
- **Manganese**: Unlike other metals, manganese readings were generally higher in samples prepared by wet digestion, except for one sample. This implies that wet digestion is more efficient for manganese extraction.
- **Copper**: Copper concentrations varied greatly between the methods. Wet digestion consistently produced detectable copper readings, whereas dry-ashing failed to detect copper in several samples. This points to the advantage of wet digestion for copper analysis.

The choice of digestion method impacts the detected concentrations of heavy metals in vegetable samples. While dry-ashing is more effective for lead, chromium, and zinc, wet digestion shows better results for manganese and copper. These findings suggest that the selection of an appropriate digestion method should be tailored to the specific metals of interest in analytical studies.
Another critical area for future work is the evaluation of other sample preparation techniques, such as microwave-assisted digestion, to compare their efficiency and accuracy with wet and dry digestion methods.

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Future Research

Future research should focus on optimizing the preparation steps for plant samples by exploring different mixtures for wet digestion and utilizing alternative types of crucibles, such as quartz crucibles, in the dry digestion process.

Expanding the range of heavy metals analyzed will help determine the most effective method for each specific metal.

Additionally, introducing the microwave digestion method, which is currently not available in Libyan chemical laboratories, will provide valuable insights into its effectiveness compared to dry and wet digestion methods in this type of analysis.

Arabic Section

المقارنة بين طريقتي الهضم الجاف والرطب في تحديد محتوى المعادن الثقيلة في الخضروات.

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الملخص: الهدف من هذه الدراسة هو المقارنة بين طريقتي الهضم الجاف (الترميد الجاف) والهضم الرطب المستخدمة في تحضير العينات من اجل تقدير تراكيز عناصر الرصاص، الكروم، الزنك، المنغنيز والنحاس في ثمان عينات من أنواع مختلفة من الخضروات. تم استخدام طريقة مطياف الامتصاص الذري (AAS) لقياس تركيزات المعادن الثقيلة بعد تحضير العينات باستخدام الطريقتين. أشارت النتائج إلى أن طريقة الهضم الجاف أعطت تركيزات أعلى للرصاص والكروم والزنك، في حين كانت طريقة الهضم الرطب أكثر فعالية للمنجنيز والنحاس. كانت قيم الانحراف المعياري النسبي (RSD%) لكلا الطريقتين متقاربة، حيث تراوحت من 0.98% إلى 2.92%.

الكلمات المفتاحية: الرماد، الجاف، الهضم الرطب، الخضار ،المعادن الثقيلة ،الامتصاص الذري

Acknowledgment

This research was supported by the Research Center of the University of Tobruk and Aman Laboratory for Chemical Analysis. Special thanks to Dr. Salah Mahjoub for his invaluable and essential assistance in the laboratory.

References

1- Liang, G., Q.Q. Wang and B.L. Huang. 2004. Concentrations of hazardous heavy metals in environmental samples collected in Xiamen, China, as determined by vapour generation non-dispersive atomic fluorescence, Analytical Science. 20: 85-88.

2- Heinz, G and P. Hautzinger. 2007. Meat processing technology, FAO, regional office for Asia and the pacific, Bangkok.

3- Maja, W., S.M. Anna and P. Pawel. 2011. Quality of the Trace Element Analysis: Sample Preparation Steps, Wide Spectra of quality Control, Dr. Isin Akyar (Ed.), ISBN: 978-953-307-683-6, InTech.
4- Rivero, R.C., P.S. Hernandez. E.M.R. Rodriquez. J.D. Martin and C.D. Romero. 2003. Mineral concentrations in cultivars of potatoes, Food Chemistry. 83: 247-253.
5- Narin, I., M. Tuzen and M. Solyak. 2004. Comparison of sample preparation procedures for the determination of heavy metals in house dust, tobacco and tea samples by atomic absorption spectrometry, Annali di Chimica (Rome).(in press).
6- Mustafa, S.,T. Mustafa .,N. Ibrahim and S. Hayati. 2004. Comparison of microwave, dry and wet digestion procedure for determination of trace contents in spice samples produced in turkey, Journal of food and drug analysis. 12(3): 245-258.
7- A. A. Yusuf, T. A. Arawolo and O. Bamgbose, (2003), Cadmium, copper and nickel levels in vegetables from industrial and residential areas of Lagos Citu, Nigeria. Food and Chemical Toxicology, pp41, 375-378.
8- AOAC. 2005. Lead, cadmium, copper, iron and zinc in foods, Atomic absorption spectrophotometry after dry ashing, AOAC international. 18th edition. USA.
9- Sneddon, J., C. Hardaway. K.K. Bobbadi and A.K. Reddy. 2006. Sample Preparation of Solid Samples for Metal Determination by Atomic Spectroscopy-An Overview and Selected Recent Applications, Applied Spectroscopy Reviews. 41(1): 1-14.