DETERMINATION OF HEAVY METALS CONTENT FROM GRAPES AND MELONS EXTRACTS♦

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Abstract: Heavy metals are natural components of the Earth's crust that cannot be degraded or destroyed. As trace elements some of them (e.g. copper, selenium, zinc) are essential to maintain the metabolism of human body, although at higher concentrations they can lead to poisoning. This work is going to present the results obtained from the determinations of grapes and melons extracts. For obtaining the extracts, Soxhlet extraction, maceration and ultrasonic method were used. A Shimadzu atomic absorption spectrometer (Model AA 6200) equipped with air – acetylene flame, was used to determine the Cu, Mn and Zn concentrations. Also, the refraction indices and relative density were measured, using an Abbé refractometer and a picnometer. The obtained results show that the highest Cu and Zn content is in the melons skin, the highest Mn content is in the grapes skin. The refraction indices and the density's values are very close to that from the Romanian standards. In the last part of this study we are

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making a comparative analysis with ours previous studies about others fruits extracts heavy metalscontent.

Keywords: *heavy metals, Soxhlet extraction, ultrasonic extraction, atomic absorption spectrometry*

INTRODUCTION

The problem of environmental pollution due to toxic metals has begun to cause concern now in most major cities. Food chain contamination by heavy metals has become an important issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. The main sources of heavy metals to vegetable crops are their growth media (soil, air, nutrient solutions) from which these are taken up by the roots or foliage [1].

Mining, manufacturing, and the use of synthetics products (pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge) can result in heavy metal contamination of urban and agricultural soils. Heavy metals also occur naturally, but rarely at toxic levels [2].

The toxicity of heavy metals is not directly proportional with their concentrations, but it also depends on the form in which they are found. Generally for the living cell, the metals found as free ions are more toxic, while the complex combinations of metals are better tolerated.

From analytical point of view, the determination of heavy metals from soil and plants imposes the use of some methods which have lowest detection limits, low matrix effects, to allow multiple-element determination and speciation analyzes [3].

Numerous research papers have been published on metals in environmental samples, such as soil, plants, water, marine sediments and organisms [4-9].

The aim of this work was to study the content of Mn, Zn and Cu in grapes and melons extracts obtained after the Soxhlet extraction, maceration or ultrasonic technique. Flame atomic absorption spectrometry (FAAS) was used for the quantitative determination of metals in these matrixes. Also, the refraction indices, relative density and conductivity were measured for the characterization of the obtained mixtures, respectively for correlation with the mineral content.

EXPERIMENTAL

Reagents and solutions

All metal stock solutions (1000 $mg.L^{-1}$) were prepared by dissolving the appropriate amounts of the spectral pure metals in dilute acids (1:1) and then diluting them with deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. All reagents were of analytical-reagent grade and all solutions were prepared using deionized water. Merck supplied the organic solvents: methanol and carbon tetrachloride; the nitric acid 65% and hydrogen peroxide 25% solutions used were of ultra pure grade.

Sample preparation

Fruits (grapes and melons) were gently washed with deionized water (to remove surface dust). 100 grams of each sample (the pulps) was submitted to conventional Soxhlet extraction respectively, to maceration (for three weeks) and ultrasonic technique.

Sample analysis

For the Soxhlet extraction the sample is placed in a thimble-holder and during operation gradually filled with condensed fresh solvent (methanol) from a distillation flask. When the liquid reaches the overflow level, a siphon aspirates the solute of the thimble-holder and unloads it back into the distillation flask, carrying the extracted analytes into the bulk liquid. This operation is repeated until complete extraction is achieved. After complete extraction the solvent was separated by the extract using vacuum distillation. We have chosen methanol because from the other studies it has been proved that the extraction power of this solvent is higher than other (CCl_4, $CHCl_3$, C_6H_6) [10]. But the solvent used to achieve the maceration of samples was carbon tetrachloride, because is lower from the point of view of toxicity. Finally was obtained approximately 50 mL of mixtures containing volatile oil. These mixtures were stored in Teflon vessels until analysis.

Another extraction of the samples was made using the ultrasonic technique. This technique used the conversion of 50-60 Hz alternating electric current in 20 kHz electric energy and its transformation in mechanic vibrations. The process that is the basis of ultrasonic technique is cavitation phenomenon. We have used an extraction installation type IUS – 150.

A Shimadzu atomic absorption spectrometer (Model AA 6200) equipped with air-acetylene flame was used for the determination of three heavy metals (Mn, Zn, Cu) from extractions and macerations. Acetylene of 99.99% purity at a flow rate of 1.8-2.0 $L.min^{-1}$ was utilized as a fuel gas and also as a carrier gas for introducing aerosols. The refraction indices and conductivity were measured using an Abbé refractometer and LF 340-A conductometer.

RESULTS AND DISCUSSION

For the characterization of studied sample obtained by extraction, maceration and ultrasonic technique, refraction indices and relative density were measured (Table 1). The values of refraction indices from literature correspond with those measured in mixtures with volatile oil obtained from grapes and melons [11]. All these values are very close to that from the Romanian standards with density between 0.850 – 1.070 $g.cm^{-3}$ and refraction indices between 1.41 – 1.61 [12-14].

***Table 1.** Values of refraction indices and relative density in the mixtures studied*

Sample	Obtaining method	Refraction indices	Relative density
Grapes extract	Soxhlet extraction	1.3954	0.906
	Maceration	1.4036	0.911
	Ultrasonic technique	1.4354	0.975
Melons extract	Soxhlet extraction	1.4302	0.895
	Maceration	1.4162	0.899
	Ultrasonic technique	1.4326	0.913

In table 2 are presented the values of conductivity for the mixtures studied. The highest value of conductivity was measured in the mixture obtained from melon's extract (1488 $\mu S.cm^{-1}$) by ultrasonic technique and the lowest value was found in grape's extract obtained by maceration (150 $\mu S.cm^{-1}$). Obtained conductivity values indicate that melons extract has a powerful electrolytic character than grapes extract.

***Table 2.** Conductivity values of obtained mixtures with volatile oil from grapes and melons*

Sample	Obtaining method	Conductivity [$\mu S.cm^{-1}$]
Grapes extract	Soxhlet extraction	154
	Maceration	150
	Ultrasonic technique	389
Melons extract	Soxhlet extraction	230
	Maceration	199
	Ultrasonic technique	1488

On the other hand the conductivity was measured for correlation with metals ions content. So, the total ionic content was higher in melons extracts than in grapes extracts (Table 3).

***Table 3.** Metal concentrations in mixtures with volatile oil obtained from studied sample by FAAS*

Sample	Obtaining method	Concentrations [$mg.kg^{-1}$] ±SD		
		Mn	Zn	Cu
Grapes extract	Soxhlet extraction	0.0156±0.0036	<LD	<LD
	Maceration	0.2395± 0.0019	0.2810±0.0025	<LD
	Ultrasonic technique	0.4905±0.0018	0.3821±0.0038	0.1183±0.0023
Melons extract	Soxhlet extraction	0.1464±0.0024	<LD	<LD
	Maceration	0.2136±0.0029	<LD	<LD
	Ultrasonic technique	0.3660±0.0030	0.5796±0.0005	0.1364±0.0039

SD – standard deviation; LD – detection limit

The highest zinc concentration was observed in melons extract (0.5796 $mg.kg^{-1}$). So, these extracts can be use like tincture, knowing the healing effect of zinc [15].
It can be notice that Cu was over the detection limit only in grapes and melons extracts obtained by ultrasonic technique.

Dobra and Viman [2] have found in some different vegetal species zinc and copper between 4.69 to 83.7 ppm, results that are higher than ours levels of Zn and Cu from fruits extracts.
Gergen and al. [16] have found in grapes: Zn - 0.97 $mg.kg^{-1}$, Mn - 1.89 $mg.kg^{-1}$ and Cu - 0.54 $mg.kg^{-1}$ values higher than ours.
May be these differences are due to different composition of soil, different fruit types, different stages of evolution and different environment conditions.
In ours previous studies [10, 17] about metals content from fruits extracts we found the same levels of these metals in different fruits extracts (figure 1), except Zn content from apples extract that is the higher value (1.23 $mg.kg^{-1}$).

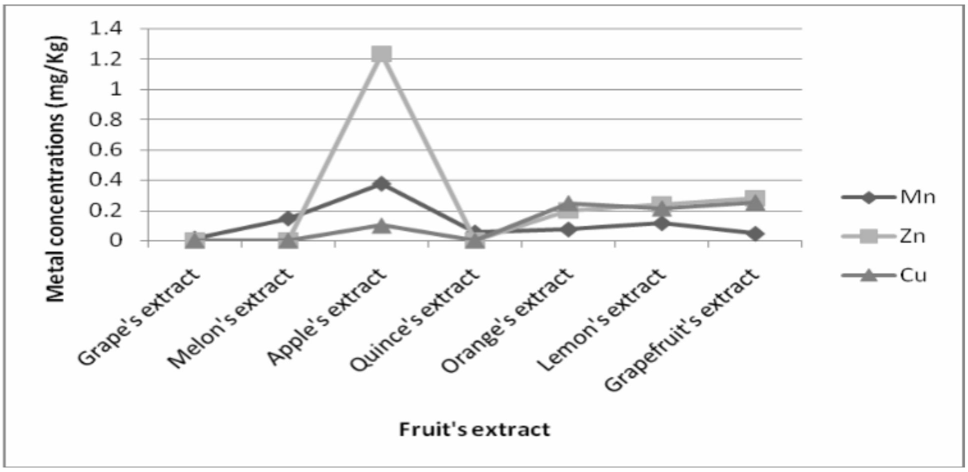

Figure 1. *Variation of metals content in different fruit's extracts*

CONCLUSIONS

The content of Mn, Zn and Cu in the grapes and melons extracts, which contains volatile oil, obtained after the Soxhlet extraction, maceration or the ultrasonic technique was studied. For all mixtures the refraction indices, the relative density and the conductivity values were measured.
The highest zinc concentration was observed in melons extract and Cu was over the detection limit only in grapes and melons extracts obtained by ultrasonic technique.
In ours previous studies about metals content from fruits extracts we found the same levels of these metals in different fruits extracts.
The determinations were made because these mixtures obtained contain volatile oil that can be used like tinctures for medical purposes, in perfumery industry and in aromatherapy treatments.

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