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Optimization and Application of Potentiometric Stripping Analysis for Determination of Heavy Metals in the samples of *Aronia melanocarpa* (Michx.) Elliot

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Lately, in the group of medicinal herbs, a significant place in the prevention and treatment of certain diseases is taken by Aronia, black chokeberry, *Aronia melanocarpa* (Michx.) Elliot, Rosaceae. Aronia is a rich source of phenolic substances, mainly flavonoids from the anthocyanin subclass which are responsible for its high antioxidant activity. In addition to the above mentioned compounds, in this plant species heavy metals such as lead and cadmium can be found in the extraction. The aim of this paper was to determine the content of Zn, Cd, Cu, and Pb in samples of fresh Aronia berries, in the juice obtained by cold washing of fresh berries, as well as in the plant material that is left behind after squashing. To determine the content of these metals in these samples, the potentiometric stripping analysis (PSA) with oxygen as an oxidant was used. Zinc and copper biometals were detected in the tested samples of Aronia (berry, juice and the rest of the Aronia berry after squeezing). The content of Zn determined ranged within the limits prescribed for this biometal, while in the tested samples the content of Cu was higher than those prescribed as recommended daily doses. In the tested Aronia samples, heavy toxic metals, lead and cadmium were also detected. The contents of these metals were low, and significantly below the content that could have harmful and toxic effects on human health. All results were confirmed by parallel ICP-OES comparative analysis . The low values for the average relative deviation (δ) indicate that there is a good agreement between the results for the content of all detected metals (Zn, Cd, Pb and Cu) obtained using the PSA technique with oxygen as an oxidant, and the ICP-OES technique.

Keywords: Medicinal plants; Aronia; Heavy metals; PSA; ICP-OES;

1. INTRODUCTION

Ever since ancient times medicinal plants have been used in the treatment of certain diseases. Moreover, some studies show that particular plant species have been used for medical treatments for more than 1000 years. According to the World Health Organization (WHO) about ¾ of the world's population relies on non-conventional medicine for its primary health care, mainly with the use of herbal remedies [1]. The use of plants in alternative medicine, such as phytotherapy, homeopathic therapy, in the prevention and alleviation of symptoms of certain diseases, has increased significantly in recent years. Increased use of these preparations compared to synthetic drugs is the result of their more favorable prices and the fact that plant-based preparations do not have serious adverse side effects on a user [2].

It is known that medicinal plants represent a rich source of active substances, such as vitamins, alkaloids, saponins, essential oils, polyphenolic compounds, which have numerous beneficial effects on the human organism [3-5]. In addition to these groups of compounds, many plant species, in their various parts (root, bark, flower, leaf, fruit, herb) contain a large number of different minerals (Na, K, Ca, Mg, Fe, Cu, Zn, Se...). They are necessary in human nutrition and have a strong effect on human health, as they are an important part of various biochemical processes in human organism [6].

Thanks to its chemical composition, medicinal plants can be used in the form of teas, tinctures or more complex phytopreparations (syrups, capsules) in therapy and disease prevention. Furthermore, active substances from plant isolates are also the starting substances for the synthesis of certain drugs. When medicinal herbs are used as an ancillary agent in therapy, it is necessary to take care that the active substance from the plant material does not interfere with a primarily used drug, causing certain problems in patients [7].

Taking into account the diversity of plants used in human nutrition or for preparing herbal preparations, constant control of their chemical composition is required. Metals such as Al, Co, Cu, Fe, Mn, Ni, and Zn are important for the development of a plant, however, if they are present in the plant above a certain level of content, they can have a detrimental effect both on the plant and on people consuming it [8]. Undesired effects of medical herbs also may result from misidentified plant species, impurities, and the presence of other contaminants such as pesticides, microbes, fertilizers and heavy metals [8]. he presence of heavy metals in the medicinal plants is conditioned by environmental factors, conditions during the process of production, storage and transport of a final product [9]. Highly toxic metals such as Pb, Cd, Hg and As can be present in medicinal herbs as contamination, and as such can be a potential source of harmful and toxic effects on humans [10]. Thus, some studies show that lead, cadmium, mercury and arsenic [6, 11-14] have been detected in medical plants from India, Malaysia, Africa, China and Brazil. Haban and associates show in their study that there have been detected certain contents of Cd, Pb and Hg in children's teas [15].

Recently, in the group of medicinal plants, Aronia, black chokeberry, *Aronia melanocarpa* (Michx.) Elliot, Rosaceae has occupied a significant place in the prevention and treatment of certain diseases. This herbal species is a rich source of various compounds that have a positive effect on human health [16]. Aronia and its products (juice, tea and various medicinal forms) are used as nutritional supplements. Aronia and Aronia products, such as juice, tea, jam, as well as various other medicinal

forms, are used as a source of food and also for the prevention and treatment of colds, cardiovascular diseases, digestive tract diseases, against viruses and bacteria [17]. Aronia fruit is a rich source of polyphenols (anthocyanins and procyanidins) and flavonoids, which have strong antioxidant action, therefore it is increasingly recommended that Aronia and its products are used to reduce the incidence of some cancers [18, 19]. According to literature, consumption of chokeberry fruits, juice and extracts have no adverse or toxic effects [20].

In addition to the above mentioned compounds, some authors' studies have shown that Aronia berry and preparations based on this plant species are a good source of various bio elements beneficial to human health [16, 21]. However, heavy metals such as lead and cadmium can be found in the extracts of this plant [16, 22]. The content of heavy metals in this plant species depends on many factors such as natural or anthropogenic contamination of the environment, geochemical characteristics of the land, and application of agro-technical measures during cultivation. Methods of producing herbal preparations (extraction, shredding, grinding, mixing and packaging), as well as transport and storage of a final product, can be a potential source of heavy metals [6]. As the use of Aronia has increased significantly recently, due to its positive effect on human health and having in mind the fact that certain heavy metals can be detected in this plant species, it is necessary to control both the plant species and its products (juice, tea, and various medical forms) to the presence of these harmful elements.

The aim of this paper is to determine the content of Zn, Cd, Cu, and Pb in samples of fresh Aronia berries, in the juice obtained by fresh berries cold squeezing, as well as in the plant material that is left behind after squashing. To determine the content of these metals in the samples, was applied the potentiometric stripping analysis (PSA) with oxygen as an oxidant, and its results were compared with the results obtained by using as the reference method optical emission spectrometry, with induced plasma (ICP-OES).

2. EXPERIMENTAL

2.1 Chemicals

The following chemicals were used for preparation and analysis of tested samples: hydrochloric acid (suprapur grade), nitric acid (65%, analytical grade), glacial acetic acid (100%, p.a. grade), acetone purchased from the Merck corporation (*Darmstadt*, Germany) and hydrogen peroxide (30%) purchased from the Fluka (Buchs, Switzerland). Standard solution of lead (1 g/L, Titrisol), standard solution of cadmium (1 g/L, Titrisol), standard solution of zinc (1 g/L, Titrisol), standard solution of gallium (1 g/L, Titrisol), standard solution of copper (1 g/L, Titrisol), and standard solution of mercury (1 g/L, Titrisol) were purchased from Merck (Darmstadt, Germany) and have been used as received.

Inductively coupled plasma (ICP) multi-element standard solution (Ultra Scientific, North Kingstown, Rhode Island, USA) of about 20.00 ± 0.10 mg/L was used as a stock solution for calibration.

Working solutions were prepared by the dilution of the standard solution with doubly distilled water with a conductivity of 0.1 μS/cm.

All containers, vessels and cells were washed with nitric acid (1:1) and doubly distilled water before use.

2.2 Samples and samples preparation

In this study, Aronia berries, juice and plant material left after squeezing the berries, are used as samples. The examined mature Aronia berries were collected from the commercial plantation, Velika Vrbnica Gornja, from the slopes of mountain Goč, Serbia. The plant has not been treated with any pesticides. The plant was identified and documented in voucher specimen collection (No 02260012) at the Institute for Medical Plant Research "Dr Josif Pančić" in Belgrade (Serbia).

Samples of Aronia berries and plant material after squeezing berries were mineralized according to a modification of the Karamethod [23] follows: as follows: an appropriate amount of Aronia Products (the products of Aronia) (3 g) was weighed accurately and transferred in acid- washed porcelain crucibles, heated gradually and maintained at 250 °C for 2 h and fired at 450 °C for 16 h in a muffle furnace. In order to complete the mineralization, ashes were then treated with 5 mL concentrated HNO_3 and 10% H_2O_2, evaporated to dryness on a steam bath and returned to the furnace at 450 °C for 1 h. The resulting ash was then treated with 5 mL concentrated HNO_3, filtered and transferred to a 25 mL volumetric flask. The solution has been rinsed with 0.5% HNO_3.

The juice was obtained by squeezing fresh, undamaged Aronia berries using an electric juicer. The juice yield (expressed as a ratio of juice weight after and weight of the fresh fruits before pressing) was 0.85. Gravimetric dry mass determination was performed in (dry-bath) at 105 ± 5^o C, until the constant mass. Dry matter expressed as percentage of original juice samples, was 85.4%.

The portion of 3 mL of analysed samples of Aronia juice was treated with a mixture of concentrated HNO_3 and HCl in a ratio of 1:1.5 (v:v), and heated at a temperature of 60-80 °C for 2 hours, in order to achieve their complete mineralisation [23].

2.3 Instrumentation

A stripping analyser M1 produced by Elektrouniverzal, Leskovac and the Faculty of Technology, Novi Sad, is a highly automated instrument for the potentiometric and chrono-potentiometric stripping analysis with microprocessor control of the complete process.

A glassy carbon (SIGRADUR-G) working electrode of a total surface area of 7.07 mm^2 was pressed into a Teflon tube (outer diameter 8 mm) at an elevated temperature. An Ag/AgCl, KCl (3.5 mol/L) electrode was used as the reference and a platinum wire as the counter electrode [24, 25].

A glassy carbon disk working electrode was used as an inert support for a mercury film. Before electrode formation, the glassy carbon surface was swept with a filter paper soaked firstly in acetone and then in doubly distilled water. A mercury film was formed electrolytically from a solution containing 100 mg/L mercury(II)-ions and 0.02 mol/L hydrochloric acid, at a constant current of 50 mA for 240 s. Once deposited, a mercury film could be used for 25–30 analyses [26].

Comparative sample analyses were carried out on iCAP 6000 inductively coupled plasma optical emission spectrometer (Thermo Scientific, Cambridge, UK) that uses an Echelle optical design and a charge injection device (CID) solid state detector.

Selected wavelengths for ICP-OES selected elements determination were 213.856 nm (Zn), 226.502 nm (Cd), 220.353 nm (Pb) and 324.754 nm (Cu).

The operational parameters for referent method, ICP-OES measurements, are given in the Table 1.

Table 1. Operational parameters for ICP-OES measurements

Parameter	
Flush Pump Rate	1.67 [Hz]
Analysis Pump Rate	0.83 [Hz]
Radio Frequency Power	1150 [W]
Nebulizer Gas Flow	0.7 [L/min]
Coolant Gas Flow	12 [L/min]
Auxiliary Gas Flow	0.5 [L/min]
Plasma View	Axial

2.4 General conditions for PSA of Zn, Cd, Pb and Cu

During the process, the PSA was modified by using oxygen as the oxidant, along with diffusion mass transfer during the analytical step. This PSA modification is the simplest one, since it uses already dissolved oxygen as the oxidant, thus reducing the contamination risk arising from the application of some externally added oxidizing agent [25].

With the PSA technique, all four elements can be determined simultaneously from the same sample. The problem with this analysis is the interference between copper and zinc because they build intermetallic compounds. This problem is solved by adding a third element that will yield the more stable intermetallic compound with the interfering element. For this purpose, a Ga (III) ion was used in this work, which with copper ions builds a more stable intermetallic compound than the compound formed between Cu and Zn. In this way, the free determination of Zn (II) ions is possible. The content of Ga (III) ions was 250 mg/L [27].

For the PSA, it was necessary that the analysed sample is in soluble form, and the pH value must be in within the range from 3.6 to 4.2. To achieve this range of pH acetate, buffer was used as the sample buffer.

In In order to define the optimal electrolysis potential, the potentials from -1.542 V to -0.652 V were examined (with respect to Ag/AgCl, 3.5 mol/L KCl) at the electrolysis time of 999 s (for Cm=1 μg/L) and 300 s (for Cm=10 μg/L). The influence of stirring rate on the determination of metals was investigated in the range of 1000 to 6000 min^{-1}. Optimal conditions for the determination of Zn, Cd, Pb and Cu were: deposition potential -1.450 V, deposition time 900 s and stirring rate 4000 rpm.

2.5 Statistical analysis

All the measurements were carried out in five repeats, and presented as the mean value. Average relative deviation was used to compare the results obtained by PSA and referent ICP-OES method. Average relative deviation was calculated with the following equation:

$$\delta = \frac{C_M(PSA) - C_M(ICP-OES)}{C_M(ICP-OES)} \times 100$$ where C_M is concetration of metals (Zn, Cd, Pb, Cu)

3. RESULTS AND DISCUSSION

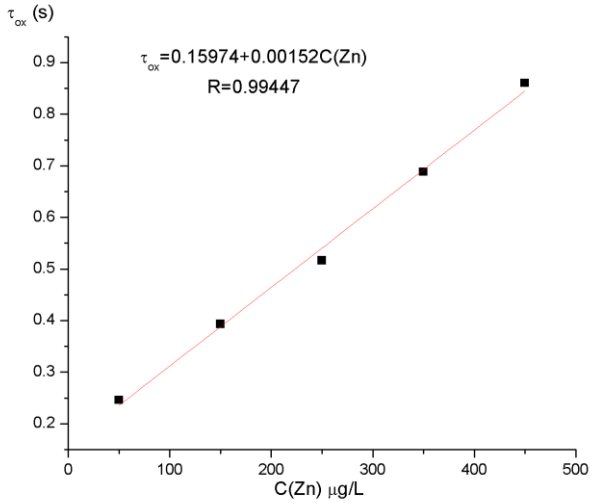

Figure 1. Linearity of the analytical signal for PSA of Zn to a model solution, of the mass concentrations of 50 to 450 µg/L

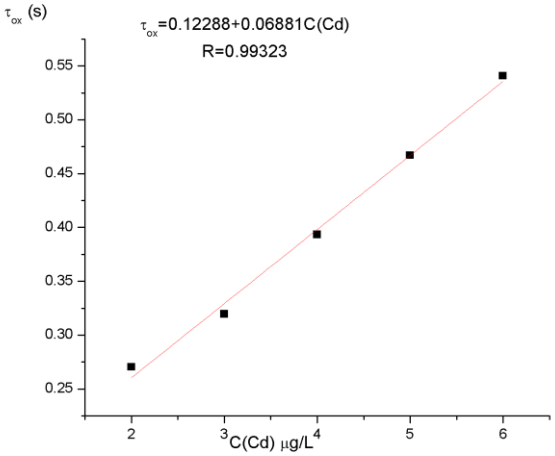

Figure 2. Linearity of the analytical signal for PSA of Cd to a model solution, of the mass concentrations of 2 to 6 µg/L

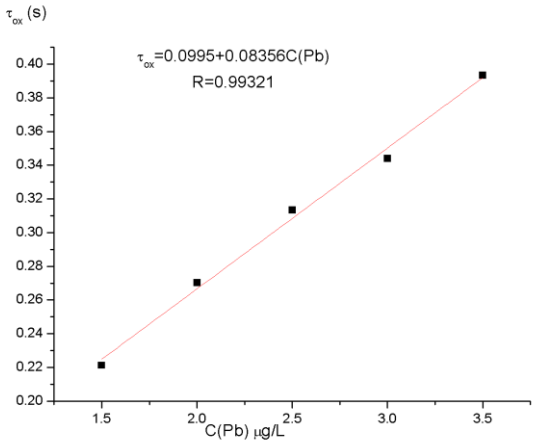

Figure 3. Linearity of the analytical signal for PSA of Pb to a model solution, of the mass concentrations of 1.5 to 3.5 μg/L

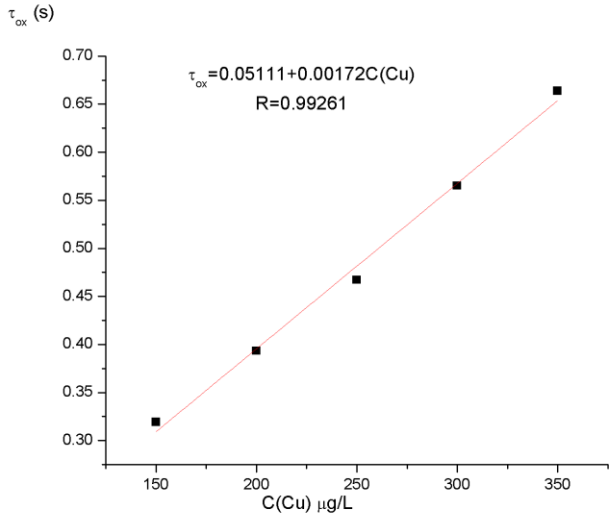

Figure 4. Linearity of the analytical signal for PSA of Cu to a model solution, of the mass concentrations of 150 to 350 μg/L

At the defined optimal conditions, the linearity and the reproducibility of the PSA analytical signal (τ_{ox} (s)) of zinc, cadmium, lead and copper in solution were checked. The analytical signal was found to be a linear function of zinc concentration within the range of 50–450 μg/L, 2-6 μg/L for cadmium, 1.5-3.5 for lead and 150-350 μg/L for copper.

Figures 1-4 show the linearity of the analytical signal of Zn, Cd, Pb and Cu as the oxidation time (τ_{ox}) dependence of concentration of each element separately.

Taking into account a high value of the correlation coefficient (R>0.99), it can be said that within the examined samples of Zn, Cd, Pb and Cu concentration range there is a very good linearity of the analytical signal.

Method of calibration curve was used for zinc, cadmium, lead and copper determination in the tested samples. In figures 1-4, equations used for determination of concentration of each element are shown.

Figure 5 shows the original instrument response record of PSA, for cadmium and lead. Since the levels of zinc and copper in the analyzed samples were significantly higher than those of Cd and Pb, the samples were diluted and separately analyzed by the PSA technique. The response signal for zinc and copper is shown in Figure 6.

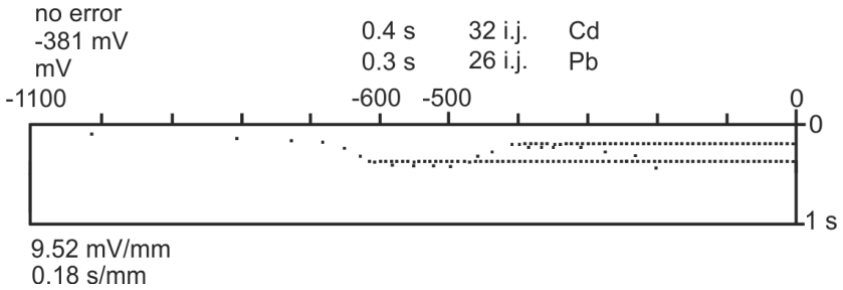

Figure 5. Original PSA response record for cadmium and lead

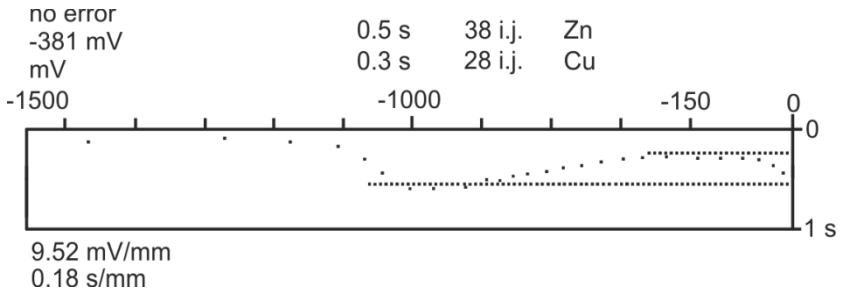

Figure 6. Original PSA response instrument record for zinc and copper

The content of Zn, Cd, Pb, and Cu of the analyzed samples by PSA and referent ICP-OES technique are shown in Table 2 and Table 3.

Table 2. The content of Zn and Cu determined by the PSA and ICP-OES technique

Sample	PSA Content of metal (mg/kg) ± SD		ICP-OES Content of metal (mg/kg) ± SD		δ_{Zn} (%)	δ_{Cu} (%)
	Zn	Cu	Zn	Cu		
Berries	3.95±0.076	2.19±0.069	3.87±0.027	2.22±0.066	1.97	-0.83
Juice	0.76±0.023	3.86±0.053	0.69±0.020	3.80±0.057	9.02	1.60
Sqm*	9.64±0.085	8.18±0.119	9.42±0.043	8.26±0.131	2.31	-0.99

*Sqm - plant material that is left behind after squashing

Table 3. The content of Pb and Cd determined by the PSA and ICP-OES technique

Sample	PSA Content of metal (mg/kg) ± SD		ICP-OES Content of metal (mg/kg) ± SD		δ_{Cd} (%)	δ_{Pb} (%)
	Cd	Pb	Cd	Pb		
Berries	0.043±0.0025	0.047±0.0018	0.047±0.0023	0.044±0.0024	-8.47	7.08
Juice	0.0043±0.0002	n.d.	0.0042±0.0002	n.d.	2.61	-
Sqm*	0.11±0.0053	0.072±0.0017	0.12±0.0046	0.074±0.0015	-7.91	-1.75

n.d. - not detected. *Sqm - plant material that is left behind after squashing

In this study, the highest concentration in all tested samples was detected for the element zinc (Table 2.). Zn is an essential element necessary for growth and development and normal functioning. Zinc is important for the regulation and coordination of the nervous system and hormones, for maintaining the structure and health of the skin and for restoring bone tissue, improving immunity, facilitating digestion, and is also necessary for protein building [28]. However, increased concentrations of zinc in the body can adversely affect human health. Certain tests have shown that increased intake of zinc in the body leads to a deficiency of copper in the liver, serum and heart, and reduced activity of copper metalloenzymes [29, 30]. Increased intake of zinc in the body may, also, have a detrimental effect on the storage of iron and can cause anemia [31].

The content of zinc in analyzed samples ranged from 0.76 to 9.64 mg/kg. The lowest content of zinc was detected in juice obtained by squeezing fresh berries, and the highest content of this element was in the material remained after obtaining the juice. The higher concentration of Zn in the remaining material can be a consequence of a process implemented for obtaining the juice. The material of electric juicer used for squeezing the fresh berries may be a reason for the increase of this element in the remaining materials of berries.

By comparing the content of Zn in the samples of berries detected in this paper (Table 2) with the content of this element in commercially available berries, ranging from 4.09 to 8.40 mg/kg [16], it can be seen that the content of zinc in berries, which are not treated with pesticides, is lower than the one found in berries for sale.

The content of Zn in samples of juice obtained by squeezing Aronia was 0.76 mg / kg. Analysis of commercial juices based on Aronia [16], shows a slightly higher zinc content compared to the natural juice samples analyzed in this paper.

The highest content of Zn is detected in the material that is left after squeezing the Aronia, which suggests that this dry material may later be used as the starting base for the preparation of tea based on Aronia, or it can be used as an additive in the production of some food and pharmaceutical preparations.

The content of zinc detected in the analyzed samples in this study suggests that the use of Aronia, as well as Aronia-based preparations, is safe both for adults and the younger population since the detected content was within the prescribed boundaries [32].

However, when it comes to the content of copper, it ranged from 2.18 to 8.18 mg/kg in the analyzed samples, which is significantly higher compared to the prescribed recommended daily doses for this metal [33].

The maximum recommended dose for adults is up to 0.9 mg per day and for children ages 4 to 8 years to 0.45 mg, therefore, for this reason, the consumption of Aronia berry must be controlled and limited to several berries daily (up to 10) and juice [34].

It is known that copper is an element that has great importance in human organism because it plays a very important role in the process of creation of red blood cells, it takes part in the mineralization and growth process of the bones, and, together with calcium, it takes part in the metabolism of phosphorus [35-37]. However, when present in the contents above prescribed it may have side effects on human health. Thus**,** high levels of copper lead to insomnia, irritability, nervous tension, and other undesired side-effects [24].

A literary examination has confirmed that some medicinal herbs contain Cu in a quantity higher than prescribed. Certain authors determine Cu in the medical herbs, and the content of copper was from

11.51 to 94.05 mg/kg [6], from 1.04 to 10.41 mg/kg [37] and from 1.96 to 19.70 mg/kg [38]. These results indicate that medicinal herbs, due to the content of copper, must have controlled usage, both because of the harmful effects that can be caused by elevated contents of this element and because of the ability of the copper to interfere with the bio metals present in the human tissue [39].

In addition to the mentioned bio metals, copper and zinc, lead and cadmium as highly toxic metals with cumulative effect, were detected in the analyzed samples. Cadmium was detected in all the analyzed samples, in contents ranging from about 0.1 to about 0.0045 mg/kg. The content of highly toxic lead metal in the Aronia berries was about 0.05 mg/kg, and in the material left behind after squeezing about 0.07 mg/kg. In juice samples, lead was not detected.

Cadmium is one of the most toxic metal ions of environment and it can be found in air, food and water. Cd ions are absorbed by most tissues of the body and deposit mainly in liver and kidney. The most dangerous characteristic of cadmium is that it accumulates throughout a lifetime. Chronic human exposure to Cd results in renal dysfunction, anemia, hepatic dysfunction, osteotoxicities, and cancer in multiple organs, potentially including the kidney [40, 41]. The toxic oral daily dose is 300 mg and the lethal is 1.5 to 8.9 g per day [42]. Cadmium is a potent human carcinogen and has been associated with cancers of the lung, prostate, pancreas, and kidney. Cadmium is a potent human carcinogen and has been associated with cancers of the lung, prostate, pancreas, and kidney. Cadmium can cause osteoporosis, anemia, non-hypertrophic emphysema, irreversible renal tubular injury, eosinophilia, anosmia and chronic rhinitis [43].

Lead is a highly toxic metal that has the property of being deposited in the tissues of vital organs (kidneys, liver, brain, lungs), bones and teeth, with its content increasing over time. According to ACDC lead levels in the blood below 240 μg/L are "normal" contents, 250-490 μg/L of moderate risk category, 500-690 μg/L of "high" risk categories and contents higher than 700 μg/L area "urgent" risk [44]. Symptoms of lead poisoning include constipation, anemia, gastrointestinal disorders, tenderness and gradual paralysis of the muscles, especially the hands, with possible cases of lethargy and malaise. Lead and lead salts can also have a carcinogenic effect, causing carcinoma of the kidney, lungs, digestive tract, bladder, brain [45].

Numerous studies have shown that the content of Cd and Pb in different samples of medicinal plants ranged from 0.01 to 2.75 mg/kg for cadmium, or from 0.046 to 9.89 mg/kg for lead [6, 14, 37, 38].

Due to the presence of these contaminants, it is necessary to monitor the content of these metals in medicinal plants. Particular attention should be paid to the presence of these metals in the herbaceous plants that grow in controlled conditions, because the content of Cd and Pb in plant material can be affected by many different factors (chemical composition of the soil, distance from the sources of this contaminant etc).

Pavlović et al. [16] have also detected certain contents of these highly toxic metals (Cd and Pb) in samples of various commercially available Aronia-based products (fruits, leaves, teas and juices). However, the detected contents, as well as the contents in this study, were significantly lower than those that could have a harmful and toxic effect on human health [42, 44].

Bearing in mind all the harmful and toxic effects that these metals can have on human body, special attention should be paid to their content, which must be determined and monitored in all samples used in human nutrition.

All results were confirmed by parallel ICP-OES comparative analysis.

Based on the values of the average relative deviation (δ) (Table 2 and Table 3), it can be said that between the results of the analyzed metals (Zn, Cd, Pb and Cu) determined by the PSA and ICP-OES technique, there is a very good correlation for all determined elements. Also, low SD values confirm the high reproducibility of analytical signals for all four determined elements. These parameters show that PSA, as a micro-analytical technique, can be used with great reliability and safety to determine and monitor the contents of these elements, both in medicinal herbs and all related samples.

PSA with oxygen as an oxidant is, in relation to other numerous techniques used in the analysis of plant material (FAAS, GFAAS, CVAAS, AFS, ICP-MS, HPLC, XRFS, NAA, and ASV) [46] significantly cheaper, faster and provides the ability to analyze one the same sample an unlimited number of times, without any degradation of the same.

4. CONCLUSION

Based on the results obtained in this study, it can be concluded that zinc and copper bio metals were detected in the tested samples of Aronia (berry, juice and the rest of the Aronia berry after squeezing). The content of Zn determined by PSA and ICP-OES technique ranged within the limits prescribed for this bio metal, while in the tested samples the content of Cu was higher than those prescribed as recommended daily doses [33]. Due to the higher content of copper in the analyzed samples, controlled consumption is recommended, both as a berry of Aronia and the juice obtained from this plant species.

In the tested Aronia samples, heavy toxic metals, lead and cadmium were also detected. The contents of these metals were low, and significantly below the content that could have harmful and toxic effects on human health. However, bearing in mind that lead and cadmium, as highly toxic metals, are deposited in the tissues of vital organs (kidneys, brain, liver, etc.) and have a cumulative effect, their content must be regularly monitored and determined, in the Aronia itself, in products based on Aronia, but also in all herbal products used in human nutrition.

The low values for the average relative deviation (δ) indicate that there is a good agreement between the results for the content of all detected metals (Zn, Cd, Pb, and Cu) obtained using the PSA technique with oxygen as an oxidant, and the ICP-OES technique. The economic accessibility, accuracy, and reliability of the PSA favor this analytical technique for analyzing plant material, in relation to both the ICP-OES and other analytical techniques, which are often applied to the analysis of samples of this type.

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