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Problem of accumulation of heavy metals in medicinal plants

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ABSTRACT

The article analyzes the content of heavy metals (cadmium, lead, copper and zinc) as priority environment pollutants as a result of human intervention, in samples of medicinal plants and soil of Mena district of Chernihiv region (Ukraine). The prospect of inversion voltammetry method for the analysis of heavy metals in medicinal plants as the highly sensitive method characterized by rapidity, good reproducibility and low equipment cost is demonstrated. A comparative analysis of the heavy metal content was carried out, bioaccumulation coefficients are calculated. It was revealed that concentration of lead and copper in the soil several times exceeds the admissible norms at the territories. It is shown that the content of copper, zinc and cadmium in the studied samples of medicinal plants doesn't exceed admissible values, while the content of lead exceeds maximum permissible concentration for the Tanacétum vulgáre L. by 4,4 times, and by 4,8 times for Hypericum perforatum L. The smallest coefficients of accumulation in all studied samples of medicinal plants were observed for cadmium. The largest lead bio-accumulation coefficients are characteristic for Tanacétum vulgáre L. and Hypericum perforatum L., which indicates the need for plant raw materials control over the content of heavy metals.

1. Introduction

One of the manifestations of human intervention on human health is the toxin presence within the environment, such as heavy metals, radionuclides, pesticides, nitrates, etc. Heavy metals, in particular zinc, copper, lead and cadmium, are of particular interest, because of their mutagenic, carcinogenic, teratogenic, embryo-, gonadotoxic impact and high bio-accumulation. Due to the intensification of the industry and agriculture in considerable territories the high concentration accumulation of these heavy metals in soils and, as a result, toxic impact on living organisms are observed.

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Soil pollution with Pb and Cd is irreversible, therefore their invading, even in insignificant quantities during a long time, leads to the accumulation of these heavy metals in soil and migration within the system “soil – plant – plant products – human body” (Bilyavsky 2012).

A toxic and hygienic characteristic of metal pollutions is important for the regulation of the content of toxic metals in the raw materials and food products. The heavy metal content has to be controlled also in medicinal plants, because there are no enough up-to-day data on the metals transition level to medicinal forms, which are made from raw materials of these plants.

The use of herbal medicinal products tends to increase around the world. Wild-growing medicinal plants are the main raw material for the production of a large number of preparations and they are mostly used without any special processing. In Ukraine, more than 45% of produced medicines are made from plants. In addition, data on element structure of medicinal plants are necessary both for the evaluation of pharmacological properties of drugs based on them and for standardization, development of analytical and normative documentation for medicinal plants.

2. Analysis of recent research

The medicinal plants ability to accumulate heavy metals from the environment has been rather widely studied during the recent decades. K.A. Dolgopolaya 2012, Y.A. Bilyavsky 2012, A.I. Samchuk 2012, S. S. Voloshchinskaya 2008 and others research the heavy metals content in soil and plants in Ukraine. However, the problem of toxic metals accumulation in wild-growing medicinal plants of Ukrainian Polissya, in particular Chernihiv region, has not been studied sufficiently. The factors influencing this process are also covered in references only fragmentary, which determines the relevance of the research in this direction.

Thus, the aim of the work was the application of electrochemical inversion voltammetry method, one of the most sensitive one to heavy metal ions, for the determination of zinc, copper, lead and cadmium content in the samples of medicinal plants from Mena district of Chernihiv region (Ukraine).

3. Methods and Materials

For determination of heavy metals concentration the samples of medicinal plants were selected: a common St. John’s Wort Hypericum perforatum L., small-leaved linden Tilia cordata Mill., wild camomile Matricaria chamomilla L., common tansy Tanacetum vulgare L. and dog rose Rosa canina L.

Medicinal plants were collected at the territory of Mena district of Chernihiv region (Ukraine). All of them belong to different botanical families and differ both by biological features and growing conditions. Medicinal plants sold in pharmacies in dried form without impurities and produced by pharmaceutical firms “Liktravy Ukrainy” and pharmaceutical factory “Viola” were also taken for control purposes.

Plants were collected in the period from May to July 2014, from 8 am to 10:00 am in dry weather. Separate parts of the plants were selected for the study: flowering bine tops of common St. John’s Wort, inflorescences of small-leaved linden, wild chamomile, common tansy; dog-rose hips. These are the parts of medicinal plants used in the official medicine to produce herbal medicinal products, so the analysis of heavy metals content in them is important.

To characterize the processes of heavy metals transformation in soil and their translocation into medicinal plants we have also selected samples of soils (according to State Standard of Ukraine DSTU 4287: 2004).

For sample preparation a programmable dual chamber furnace PDP (ПДП) (Scientific-Production Enterprise (SPE) "Tom'analyt", Russia Federation) was used. Determination of heavy metals in medicinal plants was carried out by inversion voltammetric (IV) analysis method of water solution sample on voltammetric analyzer TA-Lab (SPE "Tom'analyt", Russia Federation) in a three-electrode electrochemical cell using the software TA-lab and a modern computer.

4. Results

Samples of medicinal plants were under sample preparation using acid digestion with additives for the purpose of decomposition of matrix organic constituent and transfer of the defined elements to solution in electrochemical active form. The acid digestion was combined with a dry digestion. At first the sample was dried up for prevention of solution foaming, then processed with the concentrated nitric acid, at the next stage of a wet mineralization – mix of nitric acid and hydrogen peroxide. Thus the sample preparation time was decreased due to simultaneous use of oxidizers and oxidation at high temperature; the number of the used reactants was reduced. Administration of additives during the mineralization considerably reduced possible losses of the defined elements.

The sample of 1 g was mixed with 10 cm3 of the concentrated nitric acid in a quartz glass and then heated to the temperature of 50-60°C to the gas emission termination. Nitric acid transfers microelements into solution in the form of water soluble nitrates, eliminates chloride ions in the form of HCl and NOCl. Oxidation of organic substances only by nitric acid proceeds hard. For oxidation process acceleration the mineralization was carried out using hydrogen peroxide – added 1,5-2,0 cm3 of 30% hydrogen peroxide and evaporated to dryness within 60-70 min. at the temperature of 150-350°C. The sample was digested at the temperature of 450°C within 30 min. Operation of nitric acid and hydrogen peroxide addition, evaporation and digestion was repeated two – three times up to the homogeneous white, yellow or gray ash preparation. The ash was dissolved in 1 cm3 of formic acid and diluted with a redistillator to 10 cm3. 10 cm3 of distilled water, 0,2 cm3 of formic acid and an aliquot of 0,5 cm3 were added to a quartz electrochemical cell.

The most perspective method of the analysis of heavy metals in the environment defining zinc, copper, cadmium and lead in one sample at their joint presence is the method of inversion voltammetry. This method is characterized by high sensitivity, rapidity, good reproducibility of results and low equipment cost. Process of electrodeposition on a mercury electrode takes place at the set negative potential during the set electrolysis time. Elements electrodissolution process from the electrode surface and analytical signals registration on the voltammogram was carried out at linearly varying potential from – 1,2 to 0,05 V above silver chloride or calomel electrode at the set sensitivity. Maximum potentials of the registered anode peaks (analytical signals) of Zn, Cd, Pb, Cu against hydrochloric or formic acids are respectively (-0,9 ± 0,1)

V; (-0,6 ± 0,1) V; (-0,4 ± 0,1) V; (-0,05 ± 0,10) V. The registered maximum anode current of an element depends linearly on element concentration. Mass concentration of elements in the sample was determined by additive method of the certified element mixes.

The analysis of the tests showed that the content of zinc and copper in the studied samples of medicinal plants exceeds the content of cadmium and lead. Therefore, the separate determination on each heavy metal was used for an objective assessment of raw material quality – at first the elements with the lower contents (Cd, Pb) were defined – Fig. 1a, and then – with higher – Cu; Zn – Fig. 1b, 1c.

The typical background current-voltage curve (1), a sample of a small-leaved linden (as an example) without additive (2) and with an additive of the analyzed metal (3) is presented in Fig. 1a. During additive administration of standard solutions of zinc, cadmium, lead and copper the peak of current oxidation increases in proportion to concentration rise of these metals.

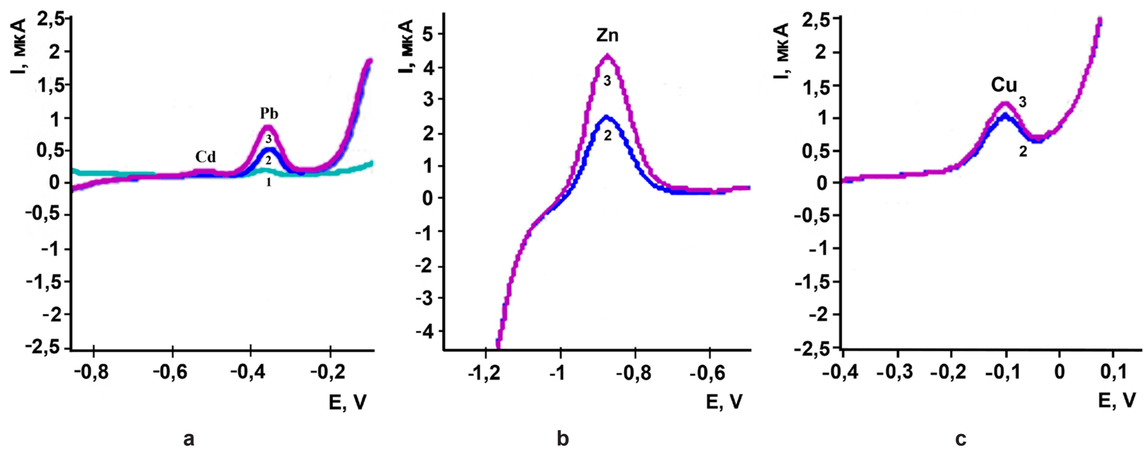

Fig 1. Typical voltammogram on the example of inflorescences of small-leaved linden (curve 1 –background, 2 – test, 3 – test with an additive)

Definition: a) Cd and Pb; b) Zn; c) Cu

Similar current-voltage curves are registered for other samples of medicinal plants. The content of heavy metals in the studied samples (tab. 1) is calculated according to the difference of current-voltage curves of test with an additive, test and background electrolyte.

Table 1. Content of heavy metals in samples of medicinal plants, mg/kg

Heavy metal	**№1**	**№2 Tília cordáta Mill.**	**№3 Matricaria chamomilla L.**	**№4 Rosa canina L.**	**№5. Tanacétum vulgáre L.**
Zn	28,00±0,01	14,00±0,02	88,00±0,06	14,00±0,01	13,00±0,01
Cd	0,0024±0,0006	0,028±0,0008	-	0,018±0,006	0,049±0,005
Pb	22,00±0,02	0,86±0,03	1,90±0,01	1,50±0,004	24,00±0,02
Cu	18,00±0,04	4,30±0,01	2,00±0,02	19,00±0,01	20,00±0,02

Analyzing samples of medicinal plants according to the content of toxic metals, we may say that the common tansy Tanacétum vulgáre L. and the St. John's Wort Hypericum perforatum L. have the greatest tendency to their accumulation. Their inflorescences contain more lead, in comparison with other samples. Copper concentration in all studied samples doesn't exceed admissible values (100 mg/kg). Cadmium content in medicinal plants doesn't exceed the maximum permissible concentration (MPC) – 0,3 mg/kg either, while the concentration of lead exceeds maximum permissible (5 mg/kg) in the samples of the St. John's Wort by 4,4 times and common tansy – by 4,8 times.

We also analyzed the content of copper, zinc, lead and cadmium in the soil of the examined territories. Concentration of elements respectively makes (mg/kg): 12,20; 22,30; 5,87 and 0,17, and MPC in the soil for mobile forms of elements are respectively (mg/kg): 3, 23; 2 and 0,7. Thus, excess of maximum permissible concentration in the soil is observed for lead and copper.

Influence of heavy metals on system "soil – plant" depends on a type and chemical properties of a pollutant, forms of heavy metals compounds in soils and their transformation, structure and properties of the soil, biological and physiological features of plants and their phenological phase. Researches of adaptation of certain types of medicinal plants grown in the polluted territories provide the opportunity to find out the invading level of heavy metals in plants. The bio-accumulation coefficient which reflects the ratio of metal content in a plant to the content of its mobile forms in the soil (Table 2) is calculated for this purpose.

Table 2. Bio-accumulation coefficients for medicinal plants

Medicinal plants	**Cu**	**Zn**	**Cd**	**Pb**
Hypericum perforatum L.	1,48	1,26	0,014	3,75
Tília cordáta Mill.	0,35	0,63	0,16	0,15
Matricaria chamomilla L.	0,16	3,9	–	0,32
Rosa canina L.	1,56	0,63	0,11	0,26
Tanacétum vulgáre L.	1,63	0,58	0,29	4,09

The analysis of heavy metals accumulation rate makes it possible to determine the following common patterns for accumulation intensity by plants: Pb>Zn>Cu>Cd. The coefficient of cadmium accumulation has the lowest values for all samples of the studied plants (from 0,014 to 0,29). The wild camomile has high coefficient of zinc accumulation. According to the conducted researches lead concentrators are Tanacétum vulgáre L. and Hypericum perforatum L. (coefficients of bio-accumulation are respectively 4,09 and 3,75), though in the previous researches (Khadanovich A.V. 2012) it was specified an insignificant coefficient of lead accumulation for the common tansy and the St. John's Wort (Gololobova A.A., 2012). It can be explained by the fact that the coefficient of biological accumulation is influenced by many factors – first of all, ecological-agrochemical characteristics of the soil, conditions during vegetation, etc. Vegetable organisms possess the whole complex of protective properties; therefore the weakened flow of the available excess chemical elements in the soil goes into bodies of assimilates. And on the contrary, the increased concentration of pollutants can be observed in plants grown on the uncontaminated soil.

5. Conclusions

Thus, the researches of adaptation of certain types of medicinal plants, grown on the contaminated and polluted land provide a possibility to determine a level of heavy metal concentration in plants. Toxic metals' influence on the "soil – plant" system depends on a type and chemical characteristics of a pollutant, forms of heavy metal compounds in soils and their transformation, soil's content and properties, biological and physiological features of plants. Inversion voltammetry method can be successfully applied to determine zinc, cadmium, lead and copper in medicinal plants and soil. An excess of permissible concentration of lead and copper in the soil was observed in the examined territories. During the collecting the medical plants' Hypericum perforatum L. and Tanacétum vulgáre L. a control over their quality for lead content is required, because they are characterized by the highest accumulative ability and high coefficients of this metal accumulation.

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