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The study of toxic and physiological elements in herbs. Analytical procedures, relationships, speciation analysis of lead and cadmium

ABSTRACT

Doctoral dissertation entitled "Study of toxic and physiological elements in herbs. Analytical procedures and relationships, speciation analysis of lead and cadmium" presents new analytical procedures for the determination of the total content of elements in herbs in conjunction with statistical and chemometric evaluation, determination of the total content of cadmium and lead in herbal extracts, which allowed the estimation of the dose of the element taken on a given exposure route and the speciation analysis of cadmium and lead in herbal extracts. New validated analytical procedures were used for the above purposes using the following techniques: ICP-ORS-MS and HPLC/ICP-DRC-MS. The study of correlations between elements was carried out using principal component analysis (PCA) and multivariate methods: canonical variable analysis (CVA) and multiple regression analysis.

Accompanied by the increasing interest in natural medicine, the requirements for the quality, safety and effectiveness of the products used are rising. In order to support the strategy of the World Health Organization WHO developed for 2014-2023, the task of which is to promote the safe use of traditional medicine, it is important to examine the composition of raw materials for the presence of elements that cause toxic effects, such as cadmium and lead, and to determine the degree of exposure to poisoning caused by consuming infusions from herbs.

Analytical quality assurance is critical to any analytical procedure. In multielement analysis, all validation parameters should be specified for each analyte to ensure reliable results. This is an important part of the research in particular for ingredients that may affect human health.

The research material consisted of dried plant parts and used herb mixtures in traditional Chinese medicine. Preparation of samples consisted in their mineralization in a closed system with microwave support and dilution or extraction with water in an incubator with shaking, dilution and filtration. Calibration solutions were prepared by appropriate dilution of the multielement standard solution. The helium or standard mode was used to determine the elements in the ICP-ORS-MS or oxygen mode in the ICP-DRC-MS. In addition, to remove the interference, the internal standard method was used, the role of which

was played by a rhodium solution. To ensure the precision and correctness of the analytical procedures, 3 certified reference materials were used: a mixture of Polish herbs, apple leaves and spinach leaves.

Determination of the total content of elements in herbs, herb roots, herbal mixtures and teas provided information that the ICP-MS technique was properly selected for the intended purpose, as evidenced by the validation results and the values of the obtained validation parameters. The conducted tests showed no deviations in the analyzed samples from the literature values, although in some samples the contents of cadmium, lead or arsenic were above the maximum permissible values. In the samples of herbs, a large range of the results of the content of the determined elements was also shown.

The chemometric analysis indicated the relationships between groups of elements, but also, as a result of the reduction of the multidimensionality of the data, made it possible to find these relationships in the tested herbs. The practical application of CVA makes it possible to monitor the composition of products from different batches and time intervals, which are also a source of variability and conclusions cannot be based only on them. Multiple regression analysis showed significant relationships between the elements: Mg - Sr, V - Pb, As - Ba, Mn - Pb, Fe - As, Fe - Ba, Co - Ni, Co - Sr, Cu - Pb, Cd - As, Zn - Pb, As - Ba.

Biological factors have an undeniable impact on the quality and safety of food. Along with it, elements are introduced into the body, both essential and as well as toxic. The assessment of the degree of risk can be formulated after identification and determination of the content of harmful factors present in nutrients. The results of determining the total content of cadmium and lead in root extracts using ICP-MS allowed to calculate the extraction efficiency of lead and cadmium, which was 5% and 23%, respectively. The doses taken in a given exposure route were estimated according to general assumptions, which may indicate an insignificant daily risk, while in the case of elements that accumulate in the body, each dose taken may have long-term negative effects on the body.

The high risk of including elements causing toxic effects in the food chain is due to the poor physiological barrier of plants and the absorption of toxic elements, as well as the development of high tolerance to their high level and poor reaction to stress initiated by the presence of metals. Speciation analysis of Chinese herb samples requires the use of selective and sensitive methods, because cadmium and lead and their compounds already in low concentrations cause toxic effects in living organisms. The determination of speciation forms of lead in a complex matrix of plant tissues means a combination of two different techniques, in which one is used to separate speciation forms, and the other is

responsible for information about the content of analytes in the samples. An important problem in the speciation analysis of lead and cadmium along with their organic and inorganic forms is the stability of these compounds throughout the analytical process and the availability of appropriate certified reference materials. The main concept of this part of the research was the development and validation of a sensitive analytical procedure for the determination of Pb^{2+} , $(\text{CH}_3)_3\text{Pb}^+$ and Cd^{2+} in samples of Chinese herbs. The subject of the research were roots, in which, according to previous research, significant amounts of lead and cadmium accumulate. Advanced high-performance liquid chromatography combined with mass spectrometry with inductively coupled plasma equipped with a dynamic reaction cell - HPLC/ICP-DRC-MS was used. The results of the optimization allowed for a very short analysis time. The resolution obtained using the selected column for Pb^{2+} and $(\text{CH}_3)_3\text{Pb}^+$ $R_s = 1,36$ was also added to the validation parameters, which is a value indicating sufficient separation of speciation forms of the same element. Linearity, limits of detection and quantification as well as precision and recovery are satisfactory. The developed procedure was applied to 10 samples of root extracts. The chemical form $(\text{CH}_3)_3\text{Pb}^+$ was not detected in any sample.