XRF METHOD APPLIED FOR RESEARCHES CONCERNING TRACE ELEMENT CONTENT OF MEDICINAL PLANTS

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Abstract

The mineral content in several medicinal plants have been measured using x-ray fluorescence spectrometry (XRFS). The medicinal herb samples of 2 g in separate containers were irradiated with the ^{109}Cd source (E_{K_α}=22.16 KeV) and ^{241}Am source (E_γ=59.57 KeV) and measured by an x-ray fluorescence detection system with a Si(Li) detector of 200 eV resolution (Fe K_α (6.4 keV). The elements as K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Bi(Pb), Se, Br employing the ^{109}Cd source and elements as Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Te, I, Ba, La, Ce, Nd, by the ^{241}Am source have been determined. All the medicinal herbs contain K, Cl, Mg, P, and Ca as minor constituents along with significant trace amounts of Cr, Cu, Fe, Mn, Se, and V. The elemental concentrations in different medicinal herbs and their biological effects on human body are discussed.

Keywords: medicinal plants, XRFS, essential elements, trace heavy metals

Introduction

Since time immemorial and in all civilizations of the world different diseases have been treated with plant medicines such as *Achillea millefolium, Chelidonium majus, Cynara scolymus, Hypericum perforatum, Tilia cordata, Matricaria recutita, and Urtíca*, which have different household names in all parts of the word. Recent scientific researches have confirmed the efficacy of many herbs and herbal preparations, some of which are remarkable effective. They offer nourishment to cells and tissues while correcting imbalances in the body's physiology over a period of time and achieve a desirable therapeutic outcome.

Accurate determination of trace concentration levels is an important task in biomedical sciences and their applications. Several experimentators have reported the analysis of the usual medicinal plants by neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS), and proton induced X-ray emission (PIXE) for up to 30 elements.

XRFS using the ^{109}Cd (E_{K_α}=22.16 keV) and ^{241}Am (E_γ=59.57 keV) radioisotope irradiation sources allows the direct measurement of the elements present in vegetable samples in μg/g range.

Specifically we investigate the application of XRFA to trace element analysis of medicinal herbs, which were analyzed in their natural composition, mixed as collective samples of 5 - 6 subsamples collected from an area of 50 x 50 m^2. The examined plants are presented in Table 1. The analytical results were further used to develop an approach of herbal medicine and formulations.

Table 1. Medicinal plant samples selected for the study

Nr.	Name	Part of plant
1	*Matricaria recutita*	Flowers
2	*Hypericum perforatum*	Flowers
3	*Achillea millefolium*	Flowers
4	*Cynara scolymus*	Leaves
5	*Tilia cordata*	Leaves, flowers
6	*Urtíca*	Leaves
7	*Chelidonium majus*	Bark

Experimental

X-ray fluorescence analysis

Samples were analyzed using an usual XRF spectrometer equipped with a Si(Li) x-ray detector having a thickness of 3 mm and an area of 30 mm^2 (Fig. 1). The measured energy resolution of the detector system was 200 eV FWHM at the 6.4 keV Fe K_α line. Analyses were made in air and the protections of Pb and Ag were meant to absorb adequately the Compton scattering effect. Photons of 22.16 keV from the ^{109}Cd source and photons of 59.57 KeV from the ^{241}Am source were used for excitation of the target x-rays. The reference materials were analyzed for data validation. The all samples were counted for 15 min and the

recorded spectra were evaluated by the etalon method using the software linked to the equipment.

In the researches conducted by XRFS we determined about 28 inorganic compounds in those medicinal plants. The detection limits of XRF method were situated between $5 \cdot 10^{-1}$ μg/g (for potassium) and $2 \cdot 10^{-4}$ μg/g (for zirconium).

Results and discussion

Following the multielemental XRFS by irradiation with ^{109}Cd source the low atomic number elements such as K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Bi(Pb), Se, Br were determined and by the use of ^{241}Am source the concentrations of the high atomic number elements such as Rb, Sr, Y, Zr, Nb, Mo, In(Cd), Sn, Te, I, Ba, La, Ce, Nd were measured.

The maximum permissible levels in raw plant material by WHO are 0.3 mg/kg for Cd, 1mg/kg for As and, respectively, 10 mg/kg for Pb. Then the sensitivity of the method for the most of the elements with the necessary experimental arrangements was enough to obtain the minimum measurable detection limits for the radioisotopes of each element, taking into account the background fluctuations (Figure 1). The system sensitivity is defined here as the number of the X-ray counts per s per μg of the corresponding element. The uncertainties of the sensitivity values measured by the source method were in the range 3.5 - 6%.

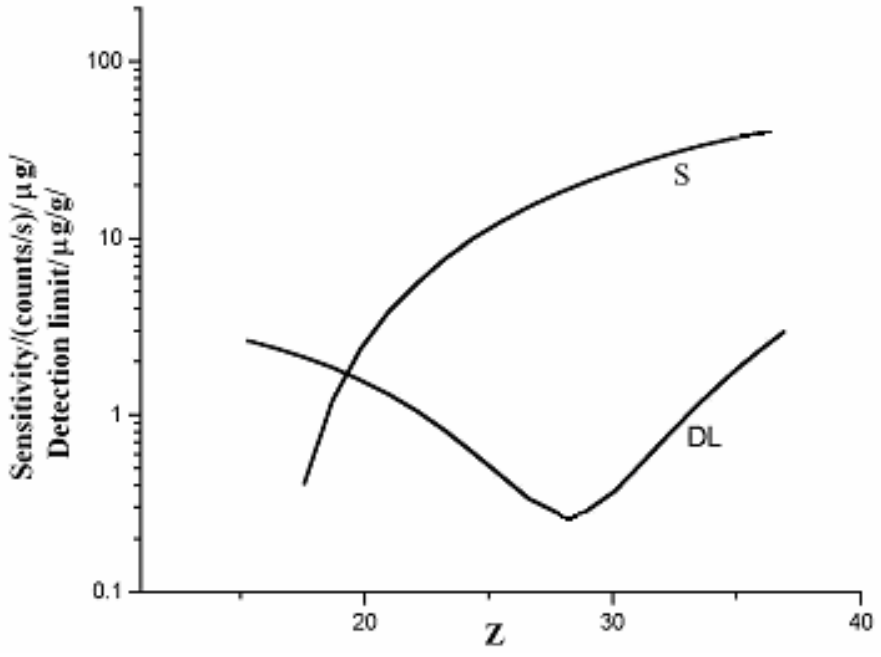

Figure 1. Sensitivity (S) and limit of detection (DL) by ^{109}Cd excitation source

Usually the trace element concentrations were higher in tree leaves than in herbs, following the order *Tilia cordata* > *Chelidonium majus* > *Cynara scolymus* > *Hypericum perforatum* > *Achillea millefolium* > *Urtíca* > *Matricaria recutita*, especially for Mn, Fe, Cu, and Rb. High K, Cl, Mg, P, and Ca contents were found in various medicinal plants. The differences are attributed to the differences in botanical structure, preferential uptake of the elements from the root soil and climatic conditions. Calcium is essential for healthy bones, teeth, blood, muscles and nerves. The most reaches medicinal plants in calcium seem to be *Tilia cordata* and *Urtíca*. Potasium is an activator of some enzymes and coenzyme for normal growth and muscle function and takes part actively in the ionic changes that occur in nerve cells during excitation and transmission of the action potential. It is mostly present in *Urtíca, Chelidonium majus* and *Matricaria recutita.*

The elements Fe, Zn and Cr are essential micronutrients for humans. Zn is relatively nontoxic and its deficiency is characterized by recurrent infections and lack of immunity; it is necessary for the growth and multiplication of the cells, for skin quality, bone metabolism and good functioning of eyesight and taste. The level of Fe in the human body is associated with hemoglobin and the transfer of oxygen from lungs to the tissue cells. Cr is found in pancreas, which produces insulin. The content of such elements was found to be particularly high in *Cynara scolymus and* also in *Hypericum perforatum* and *Matricaria recutita.*

Conclusions

A total of 28 inorganic compounds have been determined in the 7 medicinal plants commonly used in Romania using XRFS. This analytical method with multielemental characterization over a wide range of elements and minimum sample preparation is properly applied to study the medicinal plants. Elemental contents vary in a wide range, in some cases even by an order of magnitude. K, Ca, and Mg are present in mg/g amounts while Na, Fe, Zn, Cu, and Mn are found in μg/g amounts. Toxic elements as As, Cd, Hg, Pb, and Sb are present below the permissible limits. Medicinal plants contain essential and trace elements in bioavailable forms that favourable influence health and possibly increase the body's ability to ameliorate development of diseases.

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