QUANTITATIVE EVALUATION OF ESSENTIAL ELEMENTS AND TRACE HEAVY METALS IN MEDICINAL PLANTS BY PHOTON NEUTRON ACTIVATION METHOD

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Abstract

Photon neutron activation analysis (IPNAA) was employed for multielement determination of chemical content in some Romanian medicinal plants and tea infusions. The accuracy and the precision of the IPNAA method were verified by analyzing the Standard Reference Materials (SRM) IAEA-140 and Pine-SRM1575a. A good agreement between the measured concentrations of the plant constituents were obtained with errors less than 10%. Furthermore, the IPNAA technique showed a very good applicability for the determination of essential elements as well as trace elements in teas of different Romanian medicinal plant species, namely *Calendula officinalis, Rosa canina* and *Mentha.*

Keywords: IPNAA, medicinal plants, tea infusion, essential elements, heavy metals

Introduction

Medicinal plants are used throughout the world as home remedies in the traditional medicine for primary health care and raw materials for the pharmaceutical industry. They are of considerable importance in treatment of the rural and urban population too. It was surveyed that the use of herbal medicines is not so much related to socio-demographic factors, but to the availability, quality and accessibility of several health care resources. The World Health Organization (1989) established international guidelines for assessing their quality by using modern control techniques and suitable standards. The tests suppose determination of basic constituents of plants as essential elements and heavy metals, including essential heavy metals as Fe, Cu and Zn, and minor or toxic heavy metals as Pb, Cd, Sb and Hg. As usually, the medicinal plants should to be checked for the contamination with heavy metals and other toxic elements. Thus, this study is aimed to evaluate the chemical content of several medherbs and tea infusions together with the root soil by multielemental analytical method of photon neutron activation analysis. The intercorrelations between significant element concentrations and between concentration of such elements in medplant and growing soil were built.

Materials and methods

Medicinal plant samples and their root soil were collected from inhabited areas of Bucegi Mountains region and stored in sterile plastic bags during the transport to analytical laboratory. Soil samples were taken in a depth of about 0-10 cm under surface from the plant location. Tea mix from the drugstore were bought and transported in the same conditions as the collected medherbs (Table 1).

The analyses were carried out on the washed and unwashed plant material and growing soil samples with a granulation of fractions <2 mm which was previously sieved through 2-mm stainless sieve and stored in a refrigerator (0-6 ^{0}C) prior to analysis. The fresh/dry mass ratios for medicinal plants were determined (Table 1).

Table 1. Characteristics of experimental material of medicinal plant and soil samples selected for the analyses

Nr.	Name	Part of plant	Dry/fresh ratio medplant
1	*Calendula officinalis*	Flowers	7.13
2	*Rosa canina*	Fruit	4.81
3	*Mentha*	Leaves	5.20
4	*Digestive tea 1*	Medherb mix	dry mix
5	*Digestive tea 1*	Medherb mix	dry mix
6	*Antibronsic tea 1*	Medherb mix	dry mix
7	*Antibronsic tea 2*	Medherb mix	dry mix

Samples of 2 g of each sample and SRMs (IAEA-140 and Pine-SRM1575a) were used for IPNAA measurements. The analytical methodology of IPNAA at MT-25 was largely described in our previous papers [6]. The IPNAA method was suited by XRF spectrometry with X-ray radioisotope ^{109}Cd (E = 22.16 keV, $T_{1/2}$ = 453 days) and ^{241}Am (E = 59.6 keV, $T_{1/2}$ = 458 years) sources in order to assure the proper quality of the results and to determine some additional elements as Ag, Br, Cd, Cl, Fe, K, La, Nd, Pd and Sr.

To assure the validation of methods and results, procedures as sample replication and proper flux monitoring were performed, blank and standards were irradiated and measured together with samples. The deviation between the standard values and measured values was less than 5%. The sensitivity of the method for pine leaves (Pine-SRM1575a) showed a recovery of 85% for Zn, 88% for Cu and, respectively, 92% for Ni.

Results and discussion

A total of 29 chemical constituents including heavy metals (as Cd, Cu, Fe, Ni, Pb and Zn) was determined (Table 2). The results for the medplants obtained here were compared with the permissible limit values established by World Health Organization Geneva (WHO).

For the essential biological metals as Fe, Cu and Zn the highest concentrations were obtained in *Calendula officinalis*, ussualy following the order *Calendula officinalis*> *Rosa canina* > *Mentha.* As for the tea mix, the highest concentrations of the above metals were obtained in *Antibronsic tea 1* and *digestive tea 1,* while the Ni concentration has an opposite behavior. Unfortunatelly we found a big difference between the concentration of the above elements from one curative tea to another, for both type antibronsic tea and digestive tea infusions.

The highest concentration of Cd was measured in *Rosa canina,* close followed by the other two medherbs, but only in *digestive tea 2* it was somehow significant. Compared with permissible limit in Romania of 1.5 mg/kg, it was underlined that our samples are polluted to some extent.

There was a positive correlation between the Cd concentrations in the medherb and in the root soil (the ratio $c_{soil}/c_{control}$ was situated in the range 1.8 – 3.5). Some remarcable differences in concentration value were observed in washed sample material compared with that unwashed, suggesting influences from wind dust.

The concentration of Pb exhibit values under the permissible limit for all medicinal preparates investigated.

As for the other elements, significant differences among the medicinal materials studied were observed for Ba, Mo, REE, Sb, and Ti, connected with plant morphology, root soil characteristics and airborne deposition.

IPNAA concentration data obtained for important essential elements and heavy metals in medicinal plant materials can be used to evaluate their curative potentiality.

Table 2. Significant element concentrations (mg/kg) of medicinal plants and tea infusions

Element	*Calendula officinalis*	*Rosa canina*	*Mentha*	*Antibronsic tea 1*	*Antibronsic tea 2*	*Digestive tea 1*	*Digestive tea 2*
Cl			5821±624	≤800	4537±657	11891±932	
K	13283±343	9977±350	8588±300	13114±432	10156±328	13493±436	8209±346
Ca	2985±122	3881±137	5497±138	5171±175	5488±144	5476±178	6029±163
Ti	≤50	≤50	≤50	≤50	≤50	336±56	≤50
Cr	≤15	≤15	62.6±12	92±16	≤15	90±16	≤15
Mn	44±7	77±8	42±7	136±11	94±8	182±11	58±9
Fe	**344±6**	**99±5**	**86±5**	**356±8**	**142±5**	**328±8**	**198±6**
Ni	7.7±2.1	≤2.5	≤2.5	≤2.5	12.9±2.3	≤2.5	14.9±2.6
Cu	**66.0±2.1**	**81.2±2.3**	**62.0±2.1**	**101.8±2.9**	**73.1±2.2**	**104.0±3.0**	**77.6±2.4**
Zn	**17.1±1.2**	**10.7±1.2**	**13.6±1.2**	**22.7±1.7**	**18.5±1.3**	**25.2±1.7**	**19.1±1.4**
Se	≤0.7	≤0.7	≤0.7	≤0.7	≤0.7	≤0.7	≤0.7
Br	3.3±0.4		15.9±0.5	7.9±0.6	6.6±0.5	5.3±0.6	7.9±0.5
Rb	2.9±0.3	10.13±0.4	3.3±0.3	12.6±0.9	5.2±0.3	9.6±0.9	5.0±0.4
Sr	12.5±0.3	17.86±0.01	10.7±0.3	29.8±0.5	11.7±0.4	25.4±0.5	22.9±0.5
Y	0.8±0.2	≤0.3	0.6±0.2	≤0.3	1.3±0.2	≤0.3	0.5±0.3
Zr	2.2±0.2	≤0.3	0.7±0.2	≤0.3	2.2±0.2	≤0.3	1.6±0.2
Nb	1.2±0.2	≤0.2	1.0±0.2	≤0.2	1.2±0.2	≤0.2	1.3±0.2
Mo	≤0.3	≤0.3	≤0.3	3.5±0.3	≤0.3	≤0.3	≤0.3
Pd	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0
Ag	4.6±1.2	2.5±0.9	3.3±1.2	3.1±1.1	3.0±1.2	3.5±1.2	≤1.5
Cd	6.7±1.6	7.6±0.8	4.8±1.1	≤1.2	≤1.2	≤1.2	4.4±0.9
Sn	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0
Sb	9.8±1.5	≤1.0	6.7±1.0	5.5±1.0	6.4±1.2	≤1.0	3.3±0.8
Cs	≤1.0	≤1.0	4.2±1.0	≤1.0	6.0±1.2	≤1.0	≤1.0
Ba	18.8±1.7	25.5±1.0	40.2±1.4	53.7±1.3	48.6±1.6	65.9±1.5	25.4±1.1
La	7.1±1.6	3.2±0.9	3.4±1.1	≤1.0	≤1.0	≤1.0	≤1.0
Ce	8.9±1.8	≤1.5	≤1.5	5.3±1.2	7.2±1.4	≤1.5	≤1.5
Nd	≤1.5	≤1.5	≤1.5	≤1.5	≤1.5	≤1.5	≤1.5
Pb	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0

Conclusion

Three widely used medicinal herbs and two types of curative tea were analyzed for chemical content (29 elements) by IPNAA well suited by XRFS. Elemental content vary in a wide range, sometimes by an order of magnitude. Based on our results and the baseline values (WHO) a general conclusion can be drawn, that the examined medicinal plant species and tea infusions exhibited different concentrations of metals. Then a tendency among the biological materials can be observed and following from this some recommendations concerning their curative potential can be made.

References

[1] Chan, K., 2003. Chemosphere, 52:1361-1371

[2] Haider, S., Naithani, V., Barthwal, J., & Kakkar, P., 2004. Bulletin of Env. Cont. and Toxicolog., 72:119-127

[3] Kanias, G.D., Kilikoglou, V., Tsitsa, E., and Loukis, A., (1993). J. Radioanal. Nucl. Chem. 169:483.

[4] Kumar, A., Nair, A.G.C., Reddy, A.V.R., and Garg, A.N., (2005). J. Pharmacol. Biomed. Anal. 37:631.

[5] Majid, A.A.B., Sarmani, S., Yusoe, N.I, et al., (1995). J. Radioanal. Nucl. Chem. 195:173.

[6] Oprea, C., Gustova, M.V., Maslov, O.D., Belov, A.G., Oprea, I.A., Ion, I., Nedelcu, C. Pirvutoiu, M.G., Vladoiu, D., 2009. Photon neutron activation analysis of the Sea Lettuce algae from the Black Sea, Romania, Proceedings of ISINN-16, 423-429

[7] Rajurkar, N.S., Pardeshi, B.M., 1997. Appl. Rad. Isot., 48, 1059.

[8] 2. Rajurkar, N.S., Pardeshi, B.M., 1998. Appl. Rad. Isot., 49, 773.

[9 Razic, S., Onjia, A. and Potkonjak, B, 2003. J. Pharm. Biomed. Anal. 33:845

[10] WHA42.43, 1989.

[11] World Health Organization Geneva, 1998. Quality control methods for medicinal plant materials. WHO, Geneva