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RADIONUCLIDE X-RAY FLUORESCENCE ANALYSIS OF SELECTED ELEMENTS IN AGRIMONY TEA SAMPLES WITH PRECONCENTRATION

RÁDIONUKLIDOVÁ RÖNTGENOFLUORESCENČNÁ ANALÝZA VYBRANÝCH PRVKOV VO VZORKÁCH REPÍKOVÉHO ČAJU PO ZAKONCENTROVANÍ

Original research article

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Abstract

The contents of selected elements (Mn, Fe, Co, Ni, Cu, Zn, Hg and Pb) in samples of loose tea of agrimony "Repíkový čaj" (*Agrimonia eupatoria* L.) were studied in this work. Identification and determination of the selected elements content were performed using X-ray fluorescence spectrometry – the nuclear analytical method based on the interaction between low-energy gamma and X radiation and analysed substance. Solid form samples were pressed in tablets and directly analysed. Prepared infusions were analysed after the preconcentration of the elements using precipitation with thioacetamide and ammonium diethyldithiocarbamate with subsequent filtration of created precipitates through a nitrocellulose filter. Detection limits obtained from both methods were compared and their suitability for elemental analysis of plant preparations was discussed.

Slovak abstract

V práci boli skúmané obsahy vybraných prvkov (Mn, Fe, Co, Ni, Cu, Zn, Hg a Pb) vo vzorkách sypaného čaju "Repík lekársky" (*Agrimonia eupatoria* L.). Identifikácia a stanovenie obsahu vybraných prvkov boli uskutočnené za použitia rádionuklidovej röntgenofluorescenčnej spektrometrie – nukleárnej analytickej metódy založenej na interakcii medzi nízkoenegetickým gama a X žiarením a analyzovanou látkou. Vzorka pevného skupenstva boli lisované do tabliet a priamo analyzované. Pripravené zápary boli analyzované po zakoncetrovaní prvkov pomocou zrážania s tioacetamidom a dietylditiokarbamátom amónnym s následnou filtráciou vzniknutých zrazenín cez nitrocelulózový filter. Boli porovnané detekčné limity vypočítané pre obidve metódy a bola diskutovaná ich vhodnosť pre prvkovú analýzu.

INTRODUCTION

Medicinal plants can be used directly to treat various diseases: they can be used as raw material for acquiring their active constituents or for producing herbal drugs. Although the efficacy of medicinal plants for curative purposes is often assigned to their organic constituents (flavonoids, vitamins, glycosides, etc.) it has been established that there exists a relationship between the chelating of metals and some chemotherapeutic agents (Lamari et al., 2008).

Trace elements play a very important role in the formation of the active chemical constituents present in medicinal plants and are responsible for their curative as well as toxic proprieties. The role of inorganic elements in plant metabolism has long been established, but the effect and influences of these elements on the administration of medicinal plants have received relatively little attention (Desideri et al., 2010). On the other hand, health research continues to implicate metals as a possible cause of adverse human health effects based on the fact that they are actively involved in many biological processes (Okatch et al., 2012). Metals are non-biodegradable and are cumulative in nature rendering them as persistent pollutants. Several researchers have documented cases in which the metal content in plants is related to toxicity (Olowoyo et al., 2012). Asian traditional medicines have been reported to contain high levels of heavy metals such as arsenic, lead and mercury (Giacomino et al., 2011).

Different techniques were applied to determine the elemental content in the medicinal plant materials and their infusions, e.g. neutron activation analysis (Lokhande et al., 2009), inductively coupled plasma atomic emission or mass spectrometry (Wang et al. 2012; Tokalioglu, 2012), atomic absorption spectrometry (Rego et al., 2012), and various types of X-ray fluorescence spectrometry (XRFS) (Khuder et al., 2009; Desideri et al., 2010).

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The advantage of XRFS involves the polycomponent character of the analysis: the method is non-destructive, fast and accurate. The reduction of detection limit can be achieved by sample preparation. This method enables the determination of total elements content without the need of knowing their chemical state (Sýkorová et al., 2009). Analysing pharmaceuticals and plant drugs with XRFS method provides qualitative and also quantitative information of the present metal ions at very low concentration levels (ppm), either single ion or a mixture of metal ions as in most cases it may be. (Krishna Murty et al., 2005). Direct measurements of metals in biological samples by XRFS without decomposition of the matrix could not be always possible because of matrix interferences and very low concentration of metal. Coupling a preconcentration step to these methods could reduce the matrix effect, increase the sensitivity, improve detection limits and provide accurate results (Jánošová et al., 2010).

The usually applied preconcentration techniques are solvent extraction, cloud point extraction, solid phase extraction based on adsorption, electrodeposition, flotation, co-precipitation and ion exchange among others. When the preconcentration based on membrane filtration is used, a chelating agent is added to an aqueous sample containing the metal ion. In practice, the most frequently used chelating agents are diethyldithiocarbamate (Krasnodebska-Ostega et al., 2013), ammonium pyrrolidine dithiocarbamate (Giakisikli & Anthemidis, 2013), dithione and 8-hydroxyquinoline (Zhao et al., 2012).

In this work, the preconcentration based on membrane filtration is used because of its simplicity and rapidity. After the addition of the precipitating agent to an aqueous sample containing the metal ion, the created metal precipitates are collected on the surface of the membrane by filtration under the vacuum. This filter paper with adsorbed complexes is analysed by the XRFS method. Two precipitation agents, ammonium diethyldithiocarbamate (ADDC) and thioacetamide (TAA), were investigated.

EXPERIMENTAL PART

Instrumentation

The measurement of the characteristic and L-fluorescent radiation intensity of elements Mn, Fe, Co, Cu, Zn, Pb, Ni and Hg was carried out with Si/Li semiconductor detector (ÚJV Řež u Prahy, Czech Republic), thickness of beryllium window 0.25 mm, diameter of beryllium window 5 mm connected with multichannel analyzer ORTEC® and the signal was evaluated by software MAESTRO-32®. In order to excite X-rays of determined elements, radionuclide source ^{238}Pu in the form of point disk was employed (made by Amersham, activity 880 MBq, energy 12–22 keV, half-life 86.4 years). All measurements were performed in noncoaxial geometrical arrangements of source, sample and detector and the acquisition time was 2000 s.

The sample acidity was measured by means of pH-meter HI 9321 (Hanna Instruments Bratislava, Slovak Republic). Tablets were pressed on Carl Zeiss Jena 036-76.

Precipitates of metals were collected on membrane filters Pragopor 4, diameter 35 mm, size of the pore 3 μm, active area 4.91 cm^2 (Pragochema) using filtration device constructed in the Department of Pharmaceutical Analysis and Nuclear Pharmacy (Comenius University, Bratislava, Slovak Republic).

Reagents and solutions

All the reagents were of analytical grade, and deionised water was used for the preparation of all aqueous solutions of TAA (Merck Darmstadt, Germany) and ADDC (Sigma Aldrich Chemie Steinheim, Switzerland). For the pH adjustment, solutions of NaOH 1.0 mol·l^{-1} (Merck Bratislava, Slovak Republic) and HCl 35 % (Elab Nitra, Slovak Republic) were prepared. Standard solutions of Mn, Fe, Co, Ni, Cu, Zn, Hg and Pb (1 mg·ml^{-1}) were obtained from Slovak Institute of Metrology Bratislava, Slovak Republic.

Plant samples for the analysis: agrimony loose tea (Agrimonia eupatoria L.) "Repíkový čaj" (Fytopharma Malacky, Slovak Republic).

Procedure

Solid sample preparation: The agrimony tea sample of "Repíkový čaj" was weighed, ground and homogenised and then pressed into tablets (20 mm diameter, 0.3000 g) with the hydraulic press under the pressure of 10 MPa. Tablets were analysed by XRFS.

Infusion preparation: To 1 g of the agrimony tea sample, 250 ml of hot solution (90 °C) with optimal pH (3.5, 8.5 or 11.5) was added. After 15 min, the mixture was filtrated. To 30 ml of the infusion, 2.6 ml of TAA or 500 μl of 2 % solution of ADDC was added.

Standard addition of elements: To 1 g of pulverised sample in the mortar, 30 μl (i.e. 30 μg) from stock solution of Mn, Ni, Co, Pb and Hg; 50 μl (i.e. 50 μg) from stock solution of Cu, 100 μl (i.e. 100 μg) from stock solution of Zn and 200 μl (i.e. 200 μg) from stock solution of Fe were added. The mixture was dried at room temperature and homogenised and then pressed into tablets of 0.3000 g with the hydraulic press under the pressure of 10 MPa. Tablets were analysed by XRFS.

Preparation of solutions: 4 % solution of TAA and 2 % solution of ADDC were prepared.

An amount of 500 ml of deionised water was adjusted to pH values 3.5, 8.5 and 11.5 by the addition of NaOH and HCl (1 mol·l^{-1} and 0.1 mol·l^{-1}, respectively) in order to create the best pH conditions for the precipitation of the elements.

Standard solutions of analysed elements were prepared from the stock solutions of each analysed elements (1 mg·ml^{-1}) where 100 μl of the standard solution corresponded to 10 μg of the element.

Calibration curves for TAA: To 30 ml of the solution with pH 8.5 (optimal for the elements Fe, Zn, Ni and Hg) or with pH 11.5 (optimal for elements Mn, Co, Cu and Pb), 0, 100, 200, 300, 500 and 1000 μl of each element (corresponding to 0, 10, 20, 30, 50 and 100 μg of element) and 2.6 ml of 4 % solution of TAA were added.

Calibration curves for ADDC: To 30 ml of the solution with pH 3.5 (optimal for all elements), 0, 100, 200, 300, 500 and 1000 µl of each element (corresponding to 0, 10, 20, 30, 50 and 100 µg of element) and 500 µl of 2 % solution of ADDC were added. Then the mixture was stirred in the beaker for 5 min, next it was heated at 60 °C for 5 min in water bath and cooled down (10 min in ice bath). Then the mixture was filtrated through the membrane filter Pragopor 4 using the filtration device. The filter with collected precipitates was dried at the room temperature. Dried filters were analysed by XRFS. Using the same procedure and under the same conditions, a blank solution was prepared and analysed.

RESULTS AND DISCUSSION

This work was aimed to determine the presence of the elements Mn, Fe, Co, Ni, Cu, Zn, Hg and Pb by XRFS in the agrimony tea – in original solid form and its infusion after the preconcentration of the elements from the liquid phase by precipitation with TAA and ADDC.

Firstly the solid form samples were analysed. After the homogenisation, the powder was pressed into the tablets of constant parameters and these tablets were analysed with XRFS. The results are given in Table 1. The method of standard addition was applied to calculate the content of analysed elements in the sample. According to the section Procedure, the chosen amounts of each element were added to the agrimony sample and after homogenisation the pressed tablets were analysed with XRFS. Obtained counts are given in Table 2. and spectrum of the sample and the sample with added standards are presented in Fig. 1.

Detection limits (L_D) for each element present in the plant matrix were calculated as a ratio of 3σ (σ = √background noise) from the counts of non-analytical signal and counts corresponding to 1 µg of element. Detection limits are presented in Table 3. Other precision parameters such as range (R), standard deviation calculated by range (S_R), relative standard deviation for the area of peak in % (s_r) and confidence interval ($L_{1,2}$) were calculated and resulting data are given in Tables 1 and 2. The values of relative standard deviation were

Table 1. Counts corresponding to selected elements after the interaction of radionuclide source ^{238}Pu with the agrimony sample tablet

element	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
Sample No.	Counts • 2000 s^{-1} for tablets of "Repíkový čaj"							
1.	532	1027	592	408	875	1368	489	513
2.	569	1051	583	415	835	1381	505	506
3.	564	1054	613	386	878	1433	517	535
Average	**555**	**1044**	**596**	**403**	**863**	**1394**	**504**	**518**
R	37	27	30	29	43	65	28	29
s$_R$	21.86	15.95	17.72	17.13	25.40	38.40	16.54	17.13
s$_r$	3.94	1.53	2.97	4.25	2.94	2.75	3.28	3.31
L$_{1,2}$	555±48	1044±35	596±39	403±38	863±56	1384±85	504±37	518±38
background	304	500	466	355	523	774	558	542

Statistic calculation: R – range; s$_R$ – standard deviation calculate by range; s$_r$ – standard deviation for peak area in %; L$_{1,2}$ – confidence interval

Table 2. Counts corresponding to selected elements after the interaction of radionuclide source ^{238}Pu with the tablet with standard addition of elements

element	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
Sample No.	Counts • 2000 s^{-1} for tablets of "Repíkový čaj"							
1.	1069	4726	1188	1139	2304	4713	1184	1245
2.	1048	4831	1268	1115	2234	4834	1212	1319
3.	1042	4795	1179	1168	2304	4609	1207	1266
Average	**1053**	**4784**	**1212**	**1141**	**2281**	**4719**	**1201**	**1277**
R	27	105	89	53	70	225	28	74
s$_R$	15.95	62.03	52.58	31.31	41.36	132.93	16.54	43.72
s$_r$	1.51	1.30	4.34	2.74	1.81	2.82	1.38	3.42
L$_{1,2}$	1053±35	4784±137	1212±116	1141±69	2281±91	4719±293	1201±37	1277±96

Statistic calculation: R – range; s$_R$ – standard deviation calculate by range; s$_r$ – standard deviation for peak area in %; L$_{1,2}$ – confidence interval

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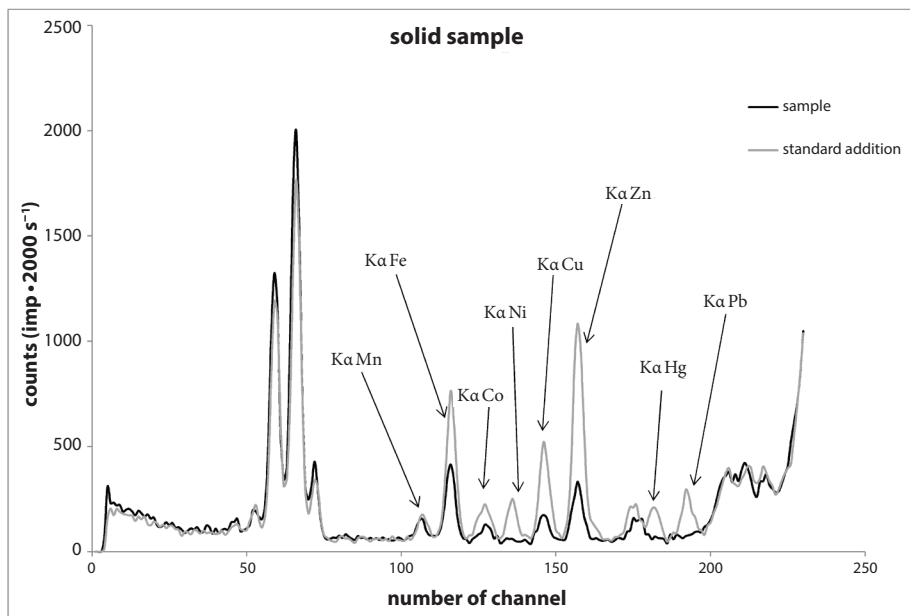TEA SAMPLES WITH PRECONCENTRATION

Figure 1. Spectrum of a tablet of agrimony tea "Repíkový čaj" and the tablet of the sample with standard addition of elements after an interaction of the radionuclide source [238]Pu.

less than 4.00 %, which confirms good reproducibility of the method and indicates suitability of the method for the practical evaluation of the plant preparations.

The resulting contents of the selected metal elements in the agrimony tea are presented in Table 3. The content of Fe was the highest among the analysed elements. The contents of Hg and Pb were under their detection limits that confirms the good quality of the plant preparation and also negligible contamination of the processed plant *Agrimonia eupatoria* L. Subsequently, the liquid samples – infusions were analysed. Before the analysis with XRFS method, the elements were preconcentrated by precipitation with TAA and ADDC reagents. Created precipitations were filtrated through Pragopor 4 filter and the enriched filters were analysed with XRFS.

Optimum pH for the multi-element analysis was chosen according to a previous study (Jánošová et al., 2010). Regarding the TAA method pH 8.5 was optimum for Fe, Ni, Zn and Hg and 11.5 for Mn, Co, Cu and Pb. When using the ADDC method, pH 3.5 was optimum for all elements. These conditions were proved to be the best for the precipitation of selected elements resulting in the lowest detection limits.

First of all, calibration curves for TAA and ADDC method were constructed. The amount of added elements was in range of 0–100 µg. The measured counts corresponded to the content of metal ions collected on the membrane filter in the form of precipitations. The linear dependence of measured signals on content of element was confirmed by calculated correlation coefficients. Parameters a and b of analytical curves in the

Table 3. Detection limits and content of the elements in the sample of "Repíkový čaj"

element	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
L_D (µg/g)	3.13	3.58	3.17	2.32	2.43	2.50	3.05	2.77
Content (µg/g)	15.12	29.09	6.33	< 2.32	11.99	18.65	< 3.05	< 2.77

Table 4. Parameters of the calibration curve in form of y = a + bx and correlation coefficient r for selected elements for TAA and ADDC method

element	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
				TAA				
a	60.05	111.67	46.88	85.66	113.36	102.85	97.46	106.29
b	-179.85	-173.49	-63.31	-92.12	180.67	-254.13	-222.91	89.29
r	0.9971	0.9982	0.9960	0.9982	0.9925	0.9974	0.9981	0.9982
				ADDC				
a	40.28	81.12	23.13	28.54	67.717	102.93	56.50	66.62
b	-11.48	-21.28	-77.88	74.98	-151.25	-282.02	-105.98	-95.67
r	0.9953	0.9980	0.9942	0.9854	0.9987	0.9981	0.9975	0.9984

form of y = a + bx and r as correlation coefficient are given in Table 4. All dependencies had linear character in chosen interval 0–100 µg. Correlation coefficient was in range of 0.9925–0.9982 for TAA method and 0.9854–0.9987 for ADDC method. The infusions were prepared according to the section *Procedure* from the solution with optimum pH 3.5 for the ADDC method and optimum pH 8.5 and 11.5 for the TAA method. Also the blank test was performed. The examples of spectrum are given in Figs. 2 and 3. Calculated detection limits along with the evaluation parameters and the content of the selected elements and using TAA and ADDC method are given in Tables 5 and 6, respectively. Using the TAA method, Fe (6.25 µg/g), Mn (5.25 µg/g) and Cu (5.33 µg/g) were determined. The contents of the other elements were under their detection limits. Using the ADDC method, Fe (6.08 µg/g) and Cu (5.25 µg/g) were determined. The contents of all other elements were under their detection limits.

The values of relative standard deviation were under 3.00 %, which confirms good reproducibility of the method and indicates suitability of the method for the practical evaluation of the plant infusions.

The detection limits of the selected elements obtained after their preconcentration with TAA were compared with the ones obtained after the preconcentration with ADDC. It was found out that TAA method combined with the XRFS analysis is the more advantageous method for the preconcentration of the selected elements Mn, Fe, Co, Ni, Cu, Hg and Pb in the plant matrices such as agrimony tea. The only exception is Zn, whose detection limits are lower in the plant matrix studied when ADDC reagent is used for the preconcentration before the XRFS analysis. However, the difference between the detection limits obtained after using the TAA method (0.62 µg/g) and the ADDC method (0.59 µg/g) was not significant.

On the other hand, capability to directly determine all selected elements in one run with relatively good sensitivity is a great advantage of the ADDC method. It is far less effective when using the TAA method. In such a case, detection limits of the majority of elements obtained by the ADDC method in one run are better than the one of the TAA method.

Finally, the content of the analysed elements in the solid plant sample of agrimony tea was compared with their content in the prepared infusion using the TAA and ADDC methods to estimate the percentage of the amount of the elements extracted into the infusion. As illustrated in Table 7, the content of the elements in the infusion is significantly lower than in the original solid plant sample. From the elements originally found in the solid sample – Mn, Fe, Co, Cu and Zn (the contents of Ni, Hg and Pb were under their detection limits) – only the presence of Mn, Fe and Cu were determined in the infusion. The best extracted element was Cu (44.45 %) when using TAA method. This low extraction can be explained by the different types of bounds between the metal elements and the organic compounds of the plant matrix which are not broken by this type of sample treatment (steeping in the hot water).

The detection limits of the analysed elements obtained using the TAA and ADDC methods of preconcentration for XRFS analysis were significantly decreased (in one order) than those in the solid plant sample of agrimony tea. Therefore, these methods can be successfully applied in the preconcentration for XRFS analysis of medicinal plant infusions.

Table 5. Content of the selected elements in the infusion using the TAA method

pH	8.5				11.5			
element	Fe	Ni	Zn	Hg	Mn	Co	Cu	Pb
R	13	4	23	4	8	4	9	5
s_R	7.68	2.36	13.59	2.36	4.73	2.36	5.32	2.96
s_r	2.99	2.41	2.81	2.48	2.67	2.43	2.51	2.55
$L_{1,2}$	257±17	98±5	484±30	95±5	177±10	97±5	212±12	116±7
L_D (µg/g)	0.36	0.33	0.62	0.29	0.58	0.60	0.32	0.30
Content (µg/g)	6.25	< 0.33	< 0.62	< 0.29	5.25	< 0.60	5.33	< 0.30

Statistic calculation: R – range; s_R – standard deviation calculate by range; s_r – standard deviation for peak area in %; $L_{1,2}$ – confidence interval

Table 6. Content of the selected elements in the infusion using the ADDC method

pH	3.5							
element	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
R	8	10	4	4	9	18	4	5
s_R	4.73	6.16	2.36	2.36	5.32	10.63	2.36	2.96
s_r	2.90	2.59	2.17	2.59	2.58	2.53	2.78	2.81
$L_{1,2}$	163±10	238±13	109±5	91±5	206±12	421±23	85±5	105±7
L_D (µg/g)	0.85	0.50	1.34	1.00	0.57	0.59	0.49	0.47
Content (µg/g)	< 0.85	6.08	< 1.34	< 1.00	5.25	< 0.59	< 0.49	< 0.47

Statistic calculation: R – range; s_R – standard deviation calculate by range; s_r – standard deviation for peak area in %; $L_{1,2}$ – confidence interval

Table 7. Content of the elements in solid sample and in the infusion of agrimony tea "Repíkový čaj" and the % of the amount of elements extracted into the infusion

Element Content (µg/g)	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb
Solid sample	15.12	29.09	6.33	< 2.32	11.99	18.65	< 3.05	< 2.77
ADDC method infusion	< 0.85	6.08	< 1.34	< 1.00	5.25	< 0.59	< 0.49	< 0.47
% of extracted elements	-	20.90	-	-	43.79	-	-	-
TAA method infusion	5.25	6.25	< 0.60	< 0.33	5.33	< 0.62	< 0.29	< 0.30
% of passed elements	34.72	21.49	-	-	44.45	-	-	-

CONCLUSION

In this work, the contents of the selected elements were studied in the samples of loose tea of agrimony "Repíkový čaj" and in its infusion. The preconcentration of the elements Mn, Fe, Co, Ni, Cu, Zn, Hg and Pb by complexation with TAA and ADDC for the XRFS method was proposed. The investigated ions were collected on the cellulose nitrate membrane filter as their complexes after the reaction with TAA or ADDC and the filter was analysed by XRFS. Calibration curve proved the linear dependence of intensity of the fluorescence radiation on the content of the metal in the sample. This method was successfully applied to the determination of the selected metals in plant matrix – agrimony tea.

Through the results obtained in this study, it is possible to conclude that the TAA and ADDC preconcentrations with precipitation, filtration on cellulose membrane and analysis of these enriched filters by XRFS significantly decrease the detection limits compared with those in solid plant samples of agrimony tea. Other benefits of the proposed TAA method are apparent from its comparison with the ADDC method. As for the detection limits, the TAA method is preferred for the majority of the elements (except for Zn, where the ADDC method was better though not significantly) when considering analysis according to the optimum pH of the analysed sample (i.e. different pH are optimum for different metals).

The advantage of this procedure is the multi-element character of the analysis, speed and the lack of need to complicate pretreatment of the sample. This method can be applied in the monitoring of metals content in solid and also liquid samples of medicinal plant and other pharmaceutical plant preparations as infusions.
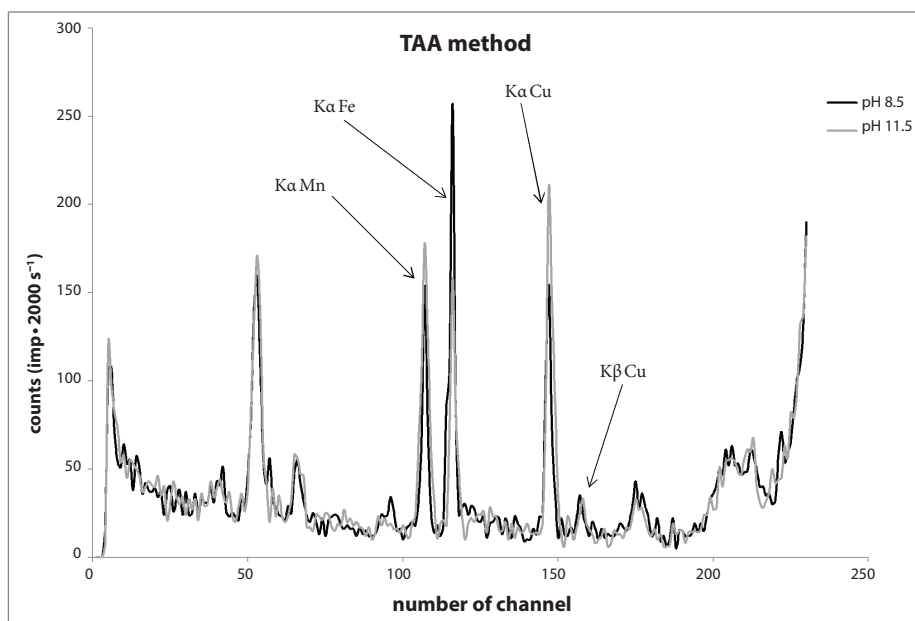
Figure 2. Spectrum of an infusion of agrimony tea "Repíkový čaj" when using the TAA method at pH 8.5 and 11.5 after an interaction of the radionuclide source [238]Pu. Abbreviations: TAA - thioacetamide
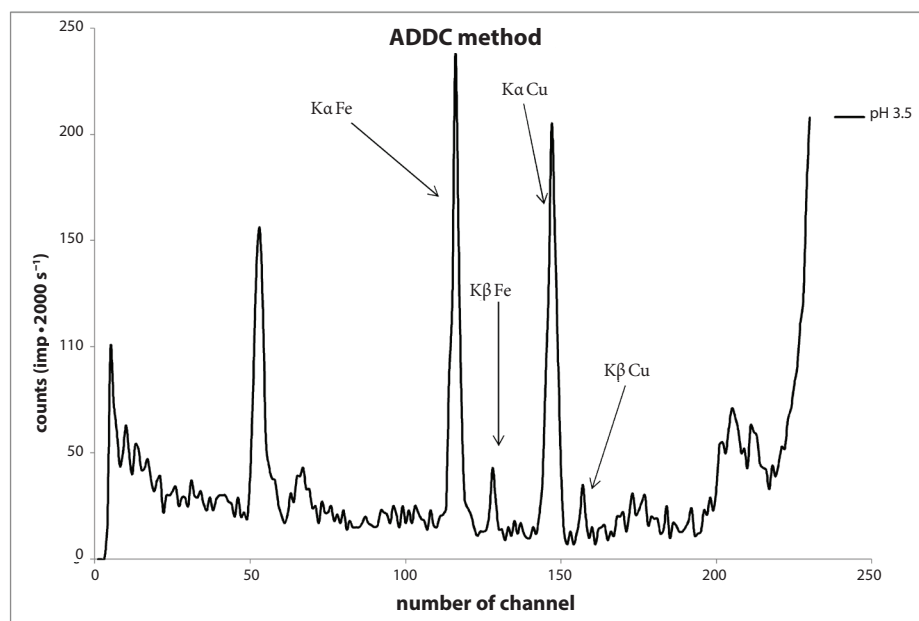
Figure 3. Spectrum of an infusion of agrimony tea "Repíkový čaj" when using the ADDC method at pH 3.5 after an interaction of the radionuclide source ^{238}Pu. Abbreviations: ADDC - ammonium diethyldithiocarbamate

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