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DETERMINATION OF LEAD, CADMIUM AND ZINC APPLYING THE STRIPPING ANALYSIS ON BIOMASS OF NATURAL GRASSLANDS

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Abstract: This study is focused on mechanisms of voltammperometric determination of lead, cadmium and zinc in the natural grassland biomass in territory of northern Kosovo, applying the Stripping analysis. Two types of determinations have been researched: individual and simultaneous research of all three metals. The preliminary researches had been conducted prior determinations on real samples defining the determination conditions: extraction potential, value of analyzed pH solution, metal extraction time, time for creating of working electrode, as well as solution mixing velocity. It was found that, with accuracy of ±2%, determinations were done for 22-900 μg dm^{-3} of lead, 16-960 μg dm^{-3} of cadmium and 18-750 μg dm^{-3} of zinc. The simultaneous metal determinations had less accurate results for lead and cadmium, whereas they ranged within accuracy limits for zinc. Heavy metal determination in biomass indicated existence of lead, cadmium and zinc in natural grasslands in northern parts of Kosovo and Metohija.

Key words: Biomass, natural grasslands, Stripping analysis, heavy metals.

Introduction

The natural grasslands are comprised of enormous variety of plant species *(Stošić et al., 2005)* and it is a very important factor in development of forage production *(Đorđević-Milošević et al., 1997)*. The growth of plant species and yields results are tightly linked to absorption of mineral elements from soil, mineral transport and distribution within the plant as well as to participation in biochemical reactions *(Jakovljević, Antić-Mladenović, 2000)*. Besides essential elements, the plants also absorb heavy metals which decrease their photosynthetic activities, mineral nutrition, protein metabolism and enzyme activity, membrane function, water regime and some other biochemical processes *(Nikolić, 2009)*. Absorption of these elements is mainly done via root where they are mainly kept if they are not

present in too high concentrations *(Bogdanović et al., 1997)*. Root epidermis represents a barrier for lead absorption, whereas zinc and cadmium are known for their great mobility through the plants and they are hardly ever kept in the root itself, which leads to slow plant growth *(Kastori et al., 2000)*.

The aim of the study is analysis of conditions and mechanisms of voltammpermetric determination of lead, cadmium and zinc in biomass, including the determination of lead, cadmium and zinc contamination levels in natural grasslands in northern part of Kosovo.

Materials and Methods

The metal content was determined applying system for the Stripping analysis, Stripping analyzer M1 (Faculty of Technical Sciences, Novi Sad and Elektrouniverzal, Leskovac, Serbia). This system functions applying three electrodes: glass carbon electrode, reference electrode (Ag/AgCl/KCl/3.5 mol dm^{-3}) and platinum wire acting as auxiliary electrode. Solutions of HCl, HNO_3 (cc), as well as standard Pb, Cd, Zn, Hg (1.000 g dm^{-3}), (suprapur), Merck (Darmstadt, Germany) and working standard solutions of: 90000 µg dm^{-3} for lead, 65000 µg dm^{-3} for cadmium and 75000 µg dm^{-3} for zinc were used.

Results for determination of lead, cadmium and zinc in standard solutions is shown on the Table 1.

Table 1. Determination of lead, cadmium and zinc in standard solutions

	Metal content			Kv (%)		S (µg)		Er (%)	
	Xs	$\overline{X}$ -p	$\overline{X}$ -i	Kv-p	Kv-i	S-p	S-i	Er-p	Er-i
Pb	4.45	4.70	4.15	12.34	14.94	0.58	0.62	5.62	-6.74
	22.48	24.98	21.90	11.34	12.02	2.52	2.58	1.12	-2.54
	44.96	45.42	43.84	11.34	11.78	5.15	5.27	1.02	-2.49
	224.3	226.6	218.54	8.01	8.51	18.15	18.61	1.03	-2.57
	447.5	452.2	434.30	7.28	7.80	32.92	33.89	1.05	-2.95
	890.8	880.6	862,79	7.26	7.64	63.93	65.93	-1.14	-3.14
Cd	3.25	3.45	3.47	13.74	14.49	0.47	0.50	6.15	6.77
	16.23	16.54	16.63	9.45	9.61	1.56	1.60	1.91	2.45
	32.47	33.09	33.25	7.54	7.67	2.49	2.55	1.90	2.41
	162.0	165.1	165.95	7.39	7.53	12.20	12.49	1.90	2.43
	323.2	329.3	330.99	7.43	7.56	24.45	25.03	1.88	2.40
	643.3	634.2	628.55	7.19	7.42	45.59	46.63	-1.41	-2.28
	960.1	941.5	936.41	7.30	7.52	68.73	70.43	-1.93	-2.47
Zn	3.75	3.97	3.99	11.59	12.28	0.46	0.49	5.86	6.40
	18.75	19.09	19.11	10.42	10.62	1.99	2.03	1.81	1.92
	37.50	38.21	38.24	10.36	10.56	3.96	4.04	1.89	1.97
	187.5	191.2	191.19	8.35	8.51	15.96	16.27	1.95	1.97
	375.0	379.8	381.85	7.43	7.53	28.22	28.74	1.27	1.83
	750.0	737.7	736.74	7.79	7.94	57.47	58.48	-1.63	-1.77

Xs-element content in standard solutions, $\overline{X}$ -average determination value–number of determinations=5, p-individual determinations, i-simultaneous determinations

The working electrode was created by extracting mercury from acid mercury(II) ion solution, content of 10 mg dm^{-3} and power of -48.90 μA during 240 seconds on surface of glass carbon. Series of 20 cm^3 water solutions and 0.5-200 μdm^3 working standards were prepared for all determinations. Extraction of heavy metals on working electrode was done individually at potential of -0.999 V for lead; -1.106 V for cadmium and -1.350 V for zinc *(Babincev et al., 2010).* Determination of all three elements simultaneously was done at potential of -1.400 V. The best results were attained for reduction time of 300 seconds, mixing velocity of 4000 min^{-1} and pH: 1.6 for lead; from 1.6 to 2.0 for cadmium and from 2.1 to 3.5 for zinc. Determination for all three elements simultaneously is most effective for pH 2.1 *(Babincev and Rajaković, 2009).*

The herbal material was collected from the natural grasslands of southern exposition of the Kopaonik mountain, at elevation of 466, 512 and 1040-1100 m from the hay stacks in September. The average samples (elevation of 1100 m) were made of average samples of nearby villages. At elevation of 466, the samples were collected from various differences from the landfills (Bostanište, Leposavić). The biomass sampling at elevation of 512 m was done in direct vicinity of the landfill (Žitkovac, Zvecan). The samples were also collected along the main road Lešak-Kosovska Mitrovica, on places 1-2 m way from the road, depending on terrain accessibility.

Following washing, the biomass was dried at 105 °C until the permanent mass was made, then it was burnt at 500 °C. One gram of ash was moisten with water and then treated with 5 cm^3 HNO_3 (cc).After evaporation, the concentrated HCl was added followed by evaporation. The remaining white mass was dissolved with 5 cm^3 HCl 2 % and prepared for analysis in a normal vessel of 100 cm^3 *(Babincev and Rajaković, 2009)*. Content of lead, cadmium and zinc was determined by standard supplements methods.

Results and Discussion

For all determinations, five measurement results were approved, based on which the average value ($\overline{X}$, μg dm^{-3}), standard deviation values (S, μg),variation coefficient (K_v, %), reproduction measure and determination error (Er, %) were calculated.

The Stripping analysis defined the metal contents of: 4-900 μg dm^{-3} for lead, 3-960 μg dm^{-3} for cadmium and 3-750 μg dm^{-3} for zinc. Both individual and simultaneous determinations of all three elements were done. Contents higher than 20 μg dm^{-3} for lead, 16 μg dm^{-3} for cadmium and 18 μg dm^{-3} for zinc were determined with ±2% of accuracy. The most accurate results of simultaneous determinations were obtained for zinc. The results of metal content determination of natural grassland biomass in northern part of Kosovo and Metohija are given in Table 2.

Lead, cadmium and zinc contents in natural grassland biomass taken form different distances from the active Trepča landfill are given in Table 3.

In researches of *Kadovića and Kneževića (2002),* the concentration of lead in actively growing grass ranged between 0.3-1.5 μg g^{-1}, 10 μg g^{-1} at the end of summer and 30 μg g^{-1} of dry mass in the end of winter.

Table 2. Content of heavy metals in biomass of natural grasslands in northern Kosmet

Locations	μg g^{-1} *SM*		
	Pb	Cd	Zn
Elevation higher than 1000 m	2.35	-	55.40
	4.56	-	78.32
	8.95	0.22	93.71
Along main road Lešak-Kosovska Mitrovica	10.32	1.62	130.24
	11.15	3.25	141.01
	12.39	6.49	135.49
In zone of passive Trepca landfill-Žitkovac	17.48	5.09	206.71
	32.94	10.12	158.55
	27.32	8.45	116.17

SM-dry material

Table 3. Content of heavy metals in biomass of natural grasslands on different distances from the active Trepca landfill-Bostanište, Leposavić

Element content μg g^{-1} SM		Distance from flotation landfil, m				
		500	750	1000	1500	3000
Determined individually	Pb	135.65	101.98	76.48	57.23	21.62
	Cd	3.90	2.11	1.96	1.18	0.74
	Zn	717.01	539.43	227.11	144.86	116.26
Determined simultaneously	Pb	130.82	98.35	73.75	55.24	20.83
	Cd	3.93	2.12	1.97	1.18	0.74
	Zn	715.98	542.41	226.79	144.89	116.28

SM-dry material

The vegetation of biomass we tested was over at the end of summer, thus the content of 10 μg g^{-1} of dry mass was anticipated. *Kabata-Pendias and Pendias (1989)*, found 0.19-9 μg g^{-1} of lead in underground parts of grasses collected from unpolluted areas, whereas there was 63-232 μg g^{-1} of lead dry mass in polluted areas. They stated that the natural lead content in plants range between 5-10 μg g^{-1} of dry mass. Our researches indicated that the grassland biomass at elevation of 1000 m contains 2-9 μg g^{-1} of lead dry mass. Absorption of lead by plants growing close to highway depends upon distance, level of biomass covering, wind speed, traffic frequency and vehicle halting time *(Filipović-Trajković et al, 2001)*. Along the main highway Kosovska Mitrovica-Lesak, the lead content in biomass was 10-12.4 μg g^{-1} of dry material. It was even 33 μg g^{-1} of dry material in grassland biomass collected directly close to passive landfill. The greatest lead content was

found in grassland biomass taken 500 m away from landfill, and it was also found in biomass taken 3000 m away from landfill.

In many plant species, the intensity of adoption of cadmium and zinc has been correlated with their concentrations in the medium. Zinc content in plants of natural grassland is different and varies in the range of 0.6 to 83 mg g^{-1} dry matter. Content of 15-30 mg g^{-1} dry matter is the border of zinc deficiency. Excess zinc from 200-500 mg g^{-1} dry matter, is rare and that in acid soils and near the mine and ore dumps *(Vukadinovic et al, 1998)*. The content of cadmium and zinc in natural grassland plants progressively decreased at different distances from the smelting of lead and zinc. Plants sampled at a distance of 750 m contained 523 mg g^{-1} dry matter of zinc. At twice the distance of zinc content was 118 mg g-1 dry matter. For the same distance cadmium content decreased from 2.1 to 0.2 mg g^{-1} dry matter *(Kastori et al., 1997)*. Biomass analyzed in this paper, a distance of 750 m from the landfill Bostanište, showed the content of 539.43 mg g^{-1} dry matter of zinc and 2.11 mg g^{-1} dry matter of cadmium. At a distance of 1500 m zinc content was 144.86 mg g^{-1} dry matter, while cadmium was 1.18 mg g^{-1} dry matter. And at a distance of 3000 m it is evident that the presence of all three metals.

Conclusion

According to the conducted tests, the increased presence of lead, cadmium and zinc in natural grassland biomass in northern Kosovo and Metohija was identified, especially on locations close to the existing polluters. In order to have the comprehensive overview of the existing polluters impact, it is necessary to conduct further researches to monitor the content of heavy metals in plant roots and soils of grasslands which take an important part in forage production in this area.

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Određivanje olova, kadmijuma i cinka striping analizom u biomasi prirodnih travnjaka

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Rezime

Ovaj rad je fokusiran na voltametrijsko određivanje olova, kadmijuma i cinka u biomasi prirodnih travnjaka. Istraživana su dva načina određivanja: svakog

metala posebno i sva tri metala istovremeno. Određivanjima u realnim uzorcima prethodila su preliminarna ispitivanja na osnovu kojih su utvrđeni uslovi određivanja: potencijali izdvajanja, pH vrednosti rastvora za analizu, potrebno vreme za izdvajanje metala, potrebno vreme za formiranje radne elektrode kao i optimalne brzine mešanja rastvora. Utvrđeno je da se, sa tačnošću od ±2%, može odrediti olovo od 22-900 μg dm^{-3}, kadmijum od 16-960 μg dm^{-3} i cink od 18-750 μg dm^{-3}. Istovremenim određivanjem metala dobijaju se manje tačni rezultati za olovo i kadmijum, a u granicama tačnosti za cink.

Određivanjem teških metala u biomasi ustanovljeno je povećano prisustvo olova, kadmijuma i cinka u prirodnim travnjacima severnog dela Kosova i Metohije.

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