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Determination of heavy metals in soil and biomass by the application of potentiometric stripping analysis

ABSTRACT

In this paper the determination of lead, cadmium and zinc in soil and biomass was performed using potentiometric stripping analysis (PSA). In order to establish the optimal experimental conditions for PSA of Pb, Cd and Zn, the influence of pH value, time of metals extraction, stirring rate of the solution and the thickness of the mercury layer, as the working electrode, was investigated. The influence of mentioned parameters was tested for individual and simultaneous metals determination. The achieved limits of determination of single ions were for: lead 22.5 μg dm^{-3}*, cadmium 16.2 μg dm*$^{-3}$ *and zinc 18.8 μg dm*$^{-3}$*. The obtained results deviated from the expected for 1.1%, 1.9% and 1.8%, for lead, cadmium and zinc, respectively.*

For simultaneous determination, the method is tested using the ions contents as follows: 45.0 μg dm^{-3} *for lead, 32.5 μg dm*$^{-3}$ *for cadmium and 37.5 μg dm*$^{-3}$ *for zinc. The relative errors for simultaneous determination were: 4.6% for lead, 1.9% for cadmium and 1.9% for zinc. For the established optimal conditions, except for lead, deviations did not exceed ±2%. It is shown that potentiometric stripping analysis is usable for individual and simultaneous determination of lead, cadmium and zinc in soil and biomass.*

Key words: *lead, cadmium, zinc, potentiometric stripping analysis, soil, biomass.*

1. INTRODUCTION

Heavy metals are naturally present in the soil from which they are mainly adopted by plants, and include in the food chain [1–3]. Although presented in traces, heavy metals are characterized by toxic effects. Testing area was the northern part of Kosovo and Metohija. This part is directly affected by 100 millions of tons of existing flotation landfills of Trepca, which occupy an area of about 350 ha. The potentiometric stripping analysis (PSA) was used to determine traces of heavy metals in a soil and biomass samples from Trepca flotation landfills surrounding [4,5]. Determination of metals by PSA is based on electrochemical reduction of the present ions and subsequent chemical oxidation of the metals deposited on the working electrode. In PSA the analytes are deposited at the mercury film as working electrode, with the constant deposition (reduction) potential, during a predetermined deposition time. Then the applied deposition potential is switched off, extracted metals are oxidized with oxygen containing in the solution, and the potential of the working electrode (measured as voltage) is measured as a function of the time [6–8]. This dependence is proportional to metal concentration. The potential of the working electrode does not change until analyzed element is oxidized. After complete oxidation of one metal, the potential of working electrode increases to the characteristic value, at which oxidation of another metal takes place [9–12].

The aim of this study was to establish optimal conditions for the individual and simultaneous PSA determination of lead, cadmium and zinc and use of PSA method for determination of these metals in real samples such as soil and grass.

2. EXPERIMENTAL

2.1. Apparatus

The experimental measurements were performed using the computerized Potentiometric Striping analyzer M1 (Faculty of Technology, Novi Sad, and Symmetry, Leskovac, Serbia). The three-electrode system was used: mercury film deposited on glassy carbon disk, with area of 7.07 mm^2,

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served as working electrode; reference electrode was silver–silver chloride electrode (Ag/AgCl/KCl//3.5 mol dm^{-3}) according to which all potentials are referred and a platinum wire as auxiliary electrode. Metals contents were determined by standard addition method.

2.2.Reagents

All the solutions were prepared from high purity chemicals (supprapur, Merck). The working solutions were prepared by diluting lead, cadmium, zinc and mercury stock standard solutions (1,000 g dm^{-3}). Concentration of working solutions were in the range from 50 to 99 mg dm^{-3} as follows: for lead 90 mg dm^{-3}, for zinc 75 mg dm^{-3}, and for cadmium 65 mg dm^{-3}. For the experiments hydrochloric acid (HCl, 30%), nitric acid (HNO_3, 65%), acetone (CH_3COCH_3, 99.5%), copper(II) sulfate ($CuSO_4$) and gallium(III) chloride ($GaCl_3$) were also used. The solutions were stored in polyethylene bottles.

2.3. Sample preparation

Soil and grass (forest biomass) samples were analyzed in this study. All analyses were carried out from aqueous solutions, which required previous sample preparation. For this purpose, 2.0 g of soil sample was dried at 105 °C to constant mass, homogenized and sieved through sieves with the openings less than 125 µm. After drying, sample of biomass was ashed at 500 °C. Dissolution of 1.0 g of dried soil sample or biomass ash was performed by digestion with concentrated nitric and chloride acid. The digested solutions were evaporated to dryness and the remaining mass was dissolved in HCl (2 mass %) and diluted to 100 cm^3 [13–16].

2.4. Procedure

Metal determination was preceded by the formation of the mercury film working electrode on the surface of glassy carbon. For this, the acidic solution of mercury(II) ion (10 mg dm^{-3}) was used and deposition was performed at a constant current of 48.90 µA for the time of 240 s. In order to achieve the optimal conditions for PSA determination of investigated metals, the series of solutions (model solutions) were prepared by adding 0.5–200 µl of working standard solutions of lead, cadmium and zinc in 20.0 cm^3 of deionized water [17]. Extraction (deposition, reduction) of lead, cadmium and zinc from the prepared model solutions was carried out at potentials of: $E_d(Pb) = -0.999$ V, $E_d(Cd) = -1.106$ V and $E_d(Zn) = -1.350$ V. The extraction potential for subsequent simultaneous determination of all three metals was more negative: $E_d(Pb, Cd, Zn) = -1.400$ V. The simultaneous determination of metals was performed after adjusting the pH and potential of extraction (reduction) because in the electrolysis of strongly acidic solutions, at the reduction potential that is more negative than −1 V, the electrochemical separation of hydrogen at the working electrode occurs. For this reason, the value of the deposition potential has to be increased for the overvoltage of hydrogen on the metals tested. Simultaneous determination of metals was carried out after addition of Ga(III) ions, in order to prevent the formation of intermetallic compounds of zinc and possibly in the sample present copper [9]. The formed Zn-Cu intermetallic compound leads to a decreasing of zinc oxidation signal, which intensity depends on the ratio of copper to zinc. Studies were performed in model solutions with zinc concentrations of: 37.5, 187.5, and 375.0 µg dm^{-3}, and copper concentrations of 10.0, 20.0, 30.0 and 35.0 µg dm^{-3}. It was found that interference in the determination of zinc can come from the copper concentrations less than 10.0 µg dm^{-3} with an error of up to 30%. By adding gallium of 40.0 µg dm^{-3} in solutions with the copper concentration of 35.0 µg dm^{-3}, and wide range of zinc concentration, the formation of Zn-Cu compound is prevented because more stable compound of gallium and copper is formed.

In order to define the optimal conditions for determination, the influence of the following parameters was particularly examined: pH value of the supporting electrolyte; stirring rate of solution, time of metals deposition and time of working electrode formation. After the optimal conditions were established, the determination of lead, cadmium and zinc in real samples of soil and biomass (grass) was performed.

3. RESULTS AND DISCUSSION

3.1. Individual metals determinations

The influence of acidity of the solution on the efficiency of determination was examined in the pH value range from 1.3–4.5. The metal concentrations were: 224.3 µg dm^{-3} (Pb), 162.0 µg dm^{-3} (Cd) and 375.0 µg dm^{-3} (Zn). It was found that the obtained results deviate by ±2% when the determinations were performed in solutions at pH 1.3, 1.6 and 2.0. The ratio of oxidation time to concentration, represented as the constant of potentiometric stripping analysis (K/s dm^3 mol^{-1}), has the highest value for Pb when determination was performed from solution pH 1.6, for Cd from solution pH 1.6 and 2.0, and for Zn from the solution pH 2.1–3.5. PSA metals determination was performed at pH 2.1, because for preset pH value, the constants of potentiometric stripping analyses for all three metals have the comparable values (Figure 1).

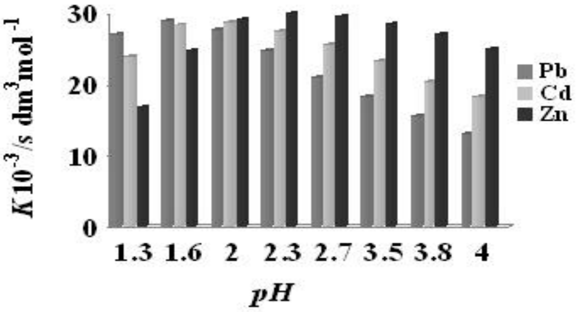

Figure. 1. Dependence of the potentiometric stripping analysis constants for determination of lead, cadmium and zinc on pH value
Slika 1. Zavisnost konstante potenciometrijske striping analize za određivanje olova, kadmijuma i cinka od pH vrednosti rastvora

The influence of stirring rate on the determination of metals was investigated in the range of 1000–6000 min^{-1}. The most efficient determinations were made at the stirring rate of 4000 min^{-1}. This can be explained as the consequence of the formation of the optimal thickness of diffusion layer at the electrode/solution surface. Metal extraction from the solution was investigated for the time of: 180, 240, 300, 360 and 420 s. The results of the determination showed that the most efficient metal extraction is achieved for the electrolysis time of 300 s. Under the mentioned conditions, the measured concentrations deviated from the expected for: 1.05%, 1.90% and 1.94% for Pb, Cd and Zn, respectively. When the minimal time employed for metal extraction is 240 s, metal contents deviated from expected by: 3.34% for lead, 3.0% for cadmium and 3.76% for zinc.

The influence of the mercury layer thickness on metal determination was analyzed as the time required for the formation of the working electrode. The working electrode formation was done by deposition the mercury on glassy carbon within: 120, 180, 240, 300 and 360 s. A good reproducibility was obtained for determination of all three ions when the mercury layer was formed within 240 s. The mercury layer formed in 240 s, based on reproducibility, provides a good homogenization of extracted metal ions, faster dissolution process and better separation.

In order to determine detection limits of potentiometric analysis for lead, cadmium and zinc, solutions of 20.0 cm^3 of deionized water and different working standard volumes from 0.5 to 600 µl were prepared. Metal extraction was performed within 300 s; solution stirring rate was 4000 min^{-1} and at the pH values of 1.6 for lead and cadmium and 2.1 for zinc. The results of determination are presented in Tables 1 - 3.

Table 1. The results of determination of lead concentration in model solutions (n=5)
Tabela 1. Rezultati određivanja koncentracije olova u model rastvorima(n=5)

Concentration of lead, µg dm^{-3}		S^c/µg	K_v^d/%	E_r^e/%
X_s^a	$\overline{X}^b$			
2.25	2.38	0.30	12.6	5.78
4.45	4.70	0.58	12.3	5.62
22.5	25.0	2.52	11.3	1.12
45.0	45.4	5.15	11.3	1.02
89.8	90.8	7.56	8.33	1.05
224	227	18.2	8.01	1.03
448	452	32.9	7.28	1.05
891	881	63.9	7.26	1.14
1319	1299	98.0	7.55	1.60
1764	1731	134	7.74	1.84
2194	2151	169	7.87	1.98
2700	2430	198	8.15	10.0

$^a X_s$-concentration of lead in the model solution, $^b\overline{X}$ - average measured concentration, $^c S$-standard deviation, $^d K_V$-coefficient of variation, $^e Er$ error of determination

Table 2. The results of determination of cadmium concentration in model solutions (n=5)
Tabela 2. Rezultati određivanja koncentracije kadmijuma u model rastvorima (n=5)

Concentration of cadmium, µg dm^{-3}		S^c/µg	K_v^d/%	E_r^e/%
X_s^a	$\overline{X}^b$			
3.25	3.45	0.47	13.7	6.15
16.2	16.5	1.56	9.45	1.91
32.5	33.1	2.49	7.54	1.90
64.9	66.1	4.98	7.53	1.89
162	165	12.2	7.39	1.90
323	329	24.5	7.43	1.88
643	634	45.6	7.19	1.41
960	941	68.7	7.30	1.93
1274	1243	106	8.51	2.40
1585	1536	137	8.64	3.04
1892	1790	156	8.72	5.42

$^a X_s$-concentration of cadmium in the model solution, $^b\overline{X}$ - average measured concentration, $^c S$-standard deviation, $^d K_V$-coefficient of variation, $^e E_r$-error of determination

From the presented results it can be seen that the minimum concentrations of lead, cadmium and zinc which can be determined with an maximal error of ± 2% (for 5 measurements) were: 22.5 µg dm^{-3} of lead (determined with an error of 1.1%), 16.2 µg dm^{-3} of cadmium (determined with an error of 1.2%) and 18.8 µg dm^{-3} of zinc (determined with an error of 1.8%). In accordance to the standard deviations and the reproducibility, these contents can be considered as the limits of determination. Standard deviations were 2.5 µg for lead, 1.6 µg for cadmium and 2.0 µg for zinc. The detection limit of potentiometric stripping analysis of lead, cadmium and zinc is about 2 µg dm^{-3}. The highest concentrations that are successfully determined by PSA were: 2190 µg dm^{-3} for lead, 960 µg dm^{-3} for cadmium, and 1300 µg dm^{-3} for zinc. These contents were determined with the error of: 2.0% for lead, 1.9% for cadmium, and 1.9% for zinc and standard deviations of: 170 µg, 70 µg and 110 µg for Pb, Cd and Zn, respectively.

Table 3. The results of determination of zinc concentration in model solutions (n=5)

Tabela 3. Rezultati određivanja koncentracije cinka u model rastvorima (n=5)

Concentration zinc, µg dm^{-3}		S^c/µg	K_v^d/%	E_r^e/%
X_s^a	$\bar{X}^b$			
1.88	2.02	0.23	11.4	7.45
3.75	3.97	0.46	11.6	5.86
18.8	19.1	2.00	10.4	1.81
37.5	38.2	3.96	10.4	1.89
188	191	16.0	8.35	1.95
375	380	28.2	7.43	1.27
750	738	57.5	7.79	1.63
1125	1106	80.8	7.30	1.65
1312	1286	111	8.68	1.95
1500	1459	131	8.95	2.76

[a]X_s-concentration of elements in the standard solution, [b]$\bar{X}$-average measured concentration, [c]S-standard deviation, [d]K_V-coefficient of variation, [e]E_r-error of determination

3.2. Simultaneous metals determinations

The simultaneous determination of investigated metals was studied in solutions containing 45.0 µg dm^{-3} of lead, 32.5 µg dm^{-3} of cadmium and 37.5 µg dm^{-3} of zinc. Results of this study have shown that applied deposition potential of the working electrode for the simultaneous determination of lead, cadmium and zinc is 490–510 mV more negative than the potential of zinc dissolution (an element with the lowest redox potential). It was found that all three elements can be determined using the –1.400 V as the deposition potential. The simultaneous determination of lead and cadmium was optimal at pH value of 1.6, while at pH 2.1, cadmium and zinc were successfully simultaneously determined. Simultaneous determination of lead and zinc was examined using solutions with pH values 1.3, 1.6, 2.0, and the most effective determinations were found at pH 2.0. Zinc is most accurately determined at pH values in the range 2.3–3.5, which may partly be explained by the qualitative properties of zinc. The simultaneous determination of all three elements was performed (with the mentioned deposition potential) at pH 2.1, as compromise value, because the PSA constants for all three metals were with the values giving enough sensitive determination. With prior pH adjustment, metal content was determined by standard addition method. The characteristic potentials of analyte oxidation are: E_{Zn} = - (0.890±10) V, E_{Cd} = - (0.595 ± 10) V and E_{Pb} = - (0.390 ± 10) V. Results of simultaneous determination of lead, cadmium and zinc are given in Table 4.

Table 4. The results of the simultaneous determination of lead, cadmium and zinc in model solution (n=5)

Tabela 4. Rezultati istovremenog određivanja olova, kadmijuma i cinka u model rastvorima (n=5)

Ion	Ion concentration, µg dm^{-3}			τ^n/s	K_p10^{-3} /s·dm^3 mol^{-1}	S^c/µg	K_v^d/%	E_r^e/%
	X_s^a	X_i^m	$\bar{X}^b$					
Pb^{2+}	45.0	44.6	42.9	1.47	32.8	5.57	13.0	4.58
		41.0		1.31	32.0			
		43.2		1.40	32.5			
		42.2		1.35	32.1			
		43.3		1.42	32.6			
Cd^{2+}	32.5	34.7	31.9	0.85	24.6	4.54	14.3	1.91
		32.1		0.79	24.6			
		29.0		0.71	24.5			
		34.0		0.84	24.8			
		29.5		0.72	24.5			
Zn^{2+}	37.5	41.9	36.8	0.90	21.6	4.47	12.1	1.89
		35.5		0.76	21.5			
		34.2		0.73	21.5			
		44.4		0.96	21.6			
		36.3		0.78	21.6			

[a]X_s-concentration of the ions in the model solution, [m]X_i-measured concentration, [b]$\bar{X}$-average measured concentration, [n]τ-time of oxidation, K_p-constant of stripping analysis, [c]S-standard deviation, [d]K_v-coefficient of variation, [e]E_r-error of determination

The obtained results suggest that there is a difference in the determinated contents when we take individual and simultaneous determinations into consideration. The results for the individual determinations deviated from the actual values by 1.0% for lead; 1.9% for cadmium and 1.9% for zinc. During the simultaneous determinations, the deviations were as follows: 4.6% for lead; 1.9% for cadmium and 1.9% for zinc. Results obtained for lead were less accurate. Since micro quantities are analysed, and relative errors of determination are less than 5%, simultaneous determination of these elements is considered possible.

3.3. Analysis of real samples

Potentiometric stripping analysis was applied for determination of heavy metals in various real samples [18–22]. In this work, lead, cadmium and zinc in soil and biomass samples are determined. Soil samples were collected at five different locations, which are at different distance from active and passive Trepca's landfills. Soil sampling was done in Jun and August of 2015. The results for individual determination of lead, cadmium and zinc in soil samples are given in Table 5. The same samples were used for simultaneous determination of analyzed metals. Results of simultaneous determination are shown in Table 6.

Table 5. The results of determination of lead, cadmium and zinc in soil (n=3)

Tabela5. Rezultati određivanja olova, kadmijuma i cinka u zemljištu (n=3)

Sampling locations	Pb		Cd		Zn	
	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%
R	158	8,24	3.70	13.7	357	7.47
G	213	8,17	6.90	9.81	519	7.65
Ž	120	8,13	34.7	7.45	226	7.58
S	129	8,03	4.90	13.7	799	7.81
K	373	7,14	23.5	8.38	334	7.54
D$_B$	2378	7,91	29.4	8.31	1201	8.05
D$_{\check{Z}}$	1119	7,62	9.30	9.75	753	7.78
MCL^q/μg g^{-1}	100.0		3.0		300.0	

^{b} $\overline{X}$ -average measured concentration; ^{d}*K$_v$*-coefficient of variation; R-Rudare; G-Grabovac; Ž-Žitkovac; S-Srbovac; K-Gornji Krnjin; D$_B$-landfill Bostanište; Dž-landfill Žitkovac, ^{q}*MCL* maximum contaminant level

Table 6. The results of the simultaneous determination of lead, cadmium and zinc in soil (n=3)

Tabela 6. Rezultati istovremenog određivanja olova, kadmijuma i cinka u zemljištu (n=3)

Sampling locations	Pb		Cd		Zn	
	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%	$\overline{X}$ ^{b}/μg g^{-1}	K_v^d/%
R	148	8.21	3.60	13.6	346	7.44
G	202	8.57	6.60	9.84	503	7.47
Ž	112	8.02	33.4	7.49	217	7.66
S	122	8.02	4.60	13.7	797	7.70
K	353	7.11	22.6	8.62	324	7.53
D$_B$	2257	7.93	28.3	8.47	1192	8.01
D$_{\check{Z}}$	1085	7.74	8.90	9.91	751	7.77
MCL^q/μg g^{-1}	100.0		3.0		300.0	

^{b} $\overline{X}$ -average measured concentration; ^{d}*K$_v$*-coefficient of variation; R-Rudare; G-Grabovac; Ž-Žitkovac; S-Srbovac; K-Gornji Krnjin; D$_B$-landfill Bostanište; D$_{\check{Z}}$-landfill Žitkovac, ^{q}*MCL* maximum contaminant level

According to the listed results, the sample from the active Trepča's landfill Bostanište has higher concentration of lead, cadmium and zinc in relation to passive Trepča's ore landfill Žitkovac. The concentration of the studied elements, at almost all investigated locations, exceeded the maximum permitted values [23]. The concentrations of metals were significantly higher in soil close to active landfill, in comparison to those in soil in the closest vicinity of a passive landfill. The lead concentration was up to twenty times higher in the active landfill. Beside the landfills, the highest concentration of lead was found in the soil of the village Gornji Krnjin, in whose closest vicinity there are both passive and active ore landfills, cadmium in soil sample from Žitkovac (close to active landfill) and zink in soil sample from Srbovac (farthest from both landfills).

Since biomass is an important factor in the nutrition chain, it is important to determine its quality, particularly in the aspect of heavy metals content [3]. The average critical and toxic heavy metal concentrations in plants are given in the literature [2]. Concentrations of lead, cadmium and zinc in samples of biomass (sampled in Jun of 2015, at a distance 200-500 m from existing landfills and along the main road Lešak–Kosovska Mitrovica, 1–2 m away from the road, depending on terrain accessibility) are presented in Table 7. The results of the simultaneous determination are given in Table 8.

Table 7. The results of the determination of lead, cadmium and zinc in biomass (n=3)

Table 7. Rezultati određivanja olova, kadmijuma i cinka u biomasi (n=3)

Sampling locations	$\overline{x}$ [b]/µg g^{-1}*DM*[y]			K_v[d]/%		
	Pb	Cd	Zn	Pb	Cd	Zn
Along main road Lešak -Kos. Mitrovica	9.70	3.60	128	12.3	13.1	8.42
	7.80	3.90	130			
	8.00	3.00	149			
Zone of passive Trepča landfill Žitkovac	26.0	7.70	169	11.6	10.3	8.53
	21.8	8.80	193			
	19.7	7.20	165			
Zone of active Trepča landfill Bostanište	134	9.60	540	8.80	10.6	8.58
	117	7.90	616			
	114	9.50	526			
Critical concentration, µg g^{-1} *DM*[y]	10 for Pb		5 for Cd		150 for Zn	
Toxic concentration, µg g^{-1}*DM*[y]	20 for Pb		10 for Cd		200 for Zn	

[b] $\overline{x}$ -average measured concentration, [y]*DM*-dry matter; [d]K_v-coefficient of variation

Table 8. The results of the simultaneous determination of lead, cadmium and zinc in biomass (n=3)

Tabela 8. Rezultati istovremenog određivanja olova, kadmijuma i cinka u biomasi (n=3)

Sampling locations	$\overline{x}$ [b]/µg g^{-1}*DM*[y]			K_v[d]/%		
	Pb	Cd	Zn	Pb	Cd	Zn
Along main road Lešak -Kos. Mitrovica	9.10	3.40	130	14.2	13.9	8.47
	7.60	3.70	133			
	6.90	2.80	152			
Zone of passive Trepča landfill Žitkovac	24.5	7.10	163	12.3	11.2	8.61
	19.7	7.30	185			
	20.2	5.90	158			
Zone of active Trepča landfill Bostanište	128	8.90	536	9.39	11.0	8.58
	111	7.10	611			
	107	8.60	522			
Critical concentration, µg g^{-1} *DM*[y]	10 for Pb		5 for Cd		150 for Zn	
Toxic concentration, µg g^{-1}*DM*[y]	20 for Pb		10 for Cd		200 for Zn	

[b] $\overline{x}$ -average measured concentration, [y]*DM*-dry matter; [d]*K_V*-coefficient of variation

Plant material samples taken along the road Lešak–Kosovska Mitrovica contained a lead concentration less than 10 µg g^{-1} of dry substance, which is about the limit of critical value. This is in good agreement with the literature data that the lead concentration in grass with active growth varied from 0.3–1.5 µg g^{-1}, increasing up to 10 µg g^{-1} at the end of the summer, while in the period of vegetation inactivity is up to 30 µg g^{-1} of dried substance [24]. The lead concentrations in the biomass collected close to the passive landfill were up to 30 µg g^{-1}, and in the zone of an active landfill 135 µg of lead was found in 1 g of dry substance (Table 8). The both values are above critical, as well as, toxic concentrations. In previous studies made on over-ground grasses on unpolluted soils, the measured lead values were from 1.2–9.0 µg, while the lead concentration in polluted soil was from 63 to 232 µg in 1 g of dry substance [25,26].

Along the road Lešak–Kosovska Mitrovica, zinc is present within the required limits, whereas its concentration in the biomass, in the vicinity of active landfill, was up to 620 µg g^{-1} of dry substance, represents a toxic concentration. The zinc content in the biomass in the vicinity of passive landfill was below the toxic but in the range of critical concentrations.

Cadmium concentration in samples taken along the Lešak-Kosovska Mitrovica road was lower than critical concentration. The cadmium concentration in biomass (impact of passive and active landfill) is in the range below toxic but above critical values.

Comparing to our earlier investigations, the obtained results indicated that contents of lead, in all analysed samples, decreased over five years, cadmium concentration near active landfill is allmost two times higher, and zinc concentration did not changed signifficantly [14].

4. CONCLUSIONS

The objective of this study is simultaneous determination of lead, cadmium and zinc by potentiometric stripping analysis, as well as its application for soil and biomass analysis. The optimal working conditions were postulated as: extraction potential was -1.400 V *vs.* Ag/AgCl,KCl electrode, extraction time was 300 s, solution stirring rate 4000 min^{-1}, pH value of the tested solution was 2.1, and time of working electrode formation was 240 s. The results of simultaneous determination are compared with the results of individual determination and quite good agreement was found. The efficiency of the individual determination was greater due to the better synchronization of the solution pH value and the extraction potential for each metal individually. The described method has wide linear working range of concentrations: (23 – 2190) µg dm^{-3} for lead, (16 – 960) µg dm^{-3} for cadmium and (19 – 1300) µg dm^{-3} for zinc. For the simultaneous determination of all three metals, relative error of determination was in the range of 2–5%. The reproducibility of PSA measurements for lead, cadmium and zinc in the soil samples was 8-10%, and in the biomass samples, the reproducibility was 8 –12% for lead, 10 – 13% for cadmium and 9% for zinc.

The obtained results indicate that potentiometric stripping analysis is usable for determination of lead, cadmium and zinc, both individually and simultaneously, as well as in the analysis of soil and biomass.

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IZVOD

ODREĐIVANJE TEŠKIH METALA U ZEMLJIŠTU I BIOMASI PRIMENOM POTENCIOMETRIJSKE STRIPING ANALIZE

U ovom radu je opisana primena potenciometrijske striping analize (PSA) za određivanje olova, kadmijuma i cinka u uzorcima zemljišta i biomase. U cilju utvrđivanja optimalnih eksperimentalnih uslova ispitivan je uticaj pH vrednosti rastvora, vremena izdvajanja metala iz rastvora, brzine mešanja rastvora i debljine filma žive, kao radne elektrode. Uticaj ovih parametara je ispitan za pojedinačno i istovremeno određivanje analiziranih metala. Postignute granice kvantifikacije pojedinačnih određivanja su za: olovo 22.5 μg dm^{-3}*, kadmijum 16.2 μg dm*$^{-3}$ *i cink 18.8 μg dm*$^{-3}$*. Dobiveni rezultati odstupaju od očekivanih vrednosti 1.1%, 1.9% i 1.8%, za olovo, kadmijum i cink, respektivno. Pri istovremenom određivanju sva tri ispitivana jona, metoda je testirana pri sledećim koncentracijama: 45.0 μg dm*$^{-3}$ *za olovo, 32.5 μg dm*$^{-3}$ *za kadmijum i 37.5 μg dm*$^{-3}$ *za cink. Relativne greške simultanog određivanja su bile: 4.6% za olovo, 1.9% za kadmijum i 1.9% za cink. Obzirom da greške određivanja ne prelaze ±2%, osim za olovo, dobijeni rezultati ukazuju da se PSA može primeniti i za istovremeno određivanje sadržaja olova, kadmijuma i cinka u zemljištu i biomasi.*

Ključne reči: *olovo, kadmijum, cink, potenciometrijska striping analiza, zemljište, biomasa.*

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