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Potentiometric Stripping Analysis of Zinc, Cadmium and Lead in Tobacco Leaves (*Nicotiana Tabacum L.*) and Soil Samples

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The potentiometric stripping analysis (PSA) with oxygen as the oxidant has been used to determine total zinc, cadmium and lead levels in tobacco leaves (*Nicotiana tabacum* L.), agricultural soil and cigarettes. The content of these metals in the leaves of the analyzed tobacco cultivars (Virginia, Burley and Oriental), obtained from locations which were close to industrial facilities and main roads, was higher than in the tobacco which was grown in rural areas. In addition to the cited potential sources of Zn, Cd and Pb, what also has an effect on the content of these metals in the studied samples of tobacco leaves is the soil in which the tobacco plant is cultivated. Thus the content of zinc in the tobacco leaves of all the studied tobacco plant types was approximately five times, of cadmium was approximately two times and lead approximately three times smaller than the content in the soil samples taken from the studied areas. The total content of heavy metals in fine brand of cigarettes was lower than in popular brand of cigarettes. The results of this work suggest that PSA may be a good method for zinc, cadmium and lead determination in soil, tobacco leaves as well as in different plant species.

Keywords: Potentiometric stripping analysis, Heavy metals (Zn, Cd and Pb), Tobacco leaves, Cigarettes, Soil

1. INTRODUCTION

Potentiometric stripping analysis (PSA) has proved to be a very useful technique for the determination of trace metals in various samples [1-4]. Although relatively simple and economic, PSA compares favorably with other methods usually employed for trace metal analysis like atomic absorption spectrophotometry (AAS), inductively coupled plasma mass spectroscopy (ICP–MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray fluorescence (XRF) and neutron-activation analysis (NAA) [4-6]. One of the common applications of PSA is zinc, cadmium and lead determination in various matrices, which is very important because their excess amounts in the body can be toxic. Heavy metals increasingly contribute to the pollution of the environment, playing an important role in the development of human illnesses and toxic effects [7-10].

Tobacco (*Nicotiana tabacum L.*) is an industrial plant which has the ability to accumulate metals. The accumulation of heavy metals in the tobacco plant is a consequence of a complex interaction between the soil, plant and animal environment. The extent of the extraction of the metals from the soil depends on the type of soil, the pH value, the chemical composition of the metal, as well as the type of tobacco [11, 12]. The fertilizers and pesticides which are used during the production of tobacco contain high concentrations of metals and represent primary factors in the pollution of agricultural soil, as well as plants [13, 14]. The research of some authors has shown that tobacco has a greater tendency towards the absorption of lead and cadmium in relation to other heavy metals [15]. The mobility of cadmium through the plant in comparison to lead is greater, so that the greatest amounts of cadmium are accumulated in the leaves, then the root and lastly in the stem of the plant [16, 17].

Tobacco smoking is a worldwide problem with 1.3 billion people currently smoking cigarettes and one person loosing life every 6 s due to tobacco related illnesses [18]. Consumption of tobacco products by both smoking and non-smoking ways affect the health of smokers directly as well as non-smokers via passive smoking and also add metal contents to the environment [19, 20].

During smoking, the heavy metal content originally present in the tobacco filler partitions among the mainstream smoke, side stream smoke, ash, and cigarette butt. Heavy metals are present in tobacco smoke and have long been associated with various diseases. Inhalation transports heavy metals in mainstream smoke through the oral cavity to the lungs. From the lungs the heavy metals are transferred to the peripheral circulation and other body organs along with other smoke constituents including addictive nicotine. Elevated cadmium levels in lung, liver, and kidney tissue [21, 22], body fat [23], blood [24] and urine [25], have been correlated with smoking history or exposure to second hand smoke. Elevated lead levels in the blood and amniotic fluid [26] and in the cord blood of newborn babies [27] have also been associated with smoking.

Elevated exposure to heavy metals from smoking contributes to increased risk for lung disease, cancer [28], and other systemic maladies such as peripheral artery disease and complications of pregnancy [29]. Cadmium and lead, which are found in tobacco smoke and elevated in smokers, have been classified as Group I and Group IIB carcinogens, respectively [30].

In addition to all these toxic heavy metals in the tobacco leaves, high contents of zinc can also be detected, considering that zinc compounds are the main constituents of artificial fertilizers, which are used during the life cycle of the plant [31].

Zinc is an essential element, necessary for the growth, development and the normal functioning of the body. Nevertheless, increased concentrations of zinc in the body can have a detrimental effect on human health. Studies have shown that the increased intake of zinc into the body can lead to a deficiency of copper in the liver, the serum and the heart, and the decrease of the activity of copper metalloenzymes [9, 10]. In addition, the increased intake of Zn into the body can have a detrimental effect on the storage of iron and can lead to the occurrence of anemia [32, 33].

Bearing in mind the cited detrimental and toxic effects of heavy metals (Zn, Cd and Pb) which can be introduced into the body through tobacco smoke, both in the case of active and passive smokers, the aim of this study was to determine the overall content of these metals in tobacco leaves and cigarettes. Considering the fact that the soil on which tobacco is cultivated is one of the main sources of the heavy metals, the content of the cited metals in the soil samples was also determined.

For the cited samples (tobacco leaves, cigarettes and soils), we defined the optimal experimental conditions under which the overall content of heavy metals was determined, by using PSA with oxygen as an oxidant [34].

2. EXPERIMENTAL

2.1. Chemicals

Hydrochloric acid (suprapur grade), a standard solution of zinc (1 g/L, Titrisol), standard solution of lead (1 g/L, Titrisol), standard solution of cadmium (1 g/L, Titrisol) and standard solution of mercury (1 g/L, Titrisol) were purchased from the Merck corporation (Darmstadt, Germany), and were used in the same state they were received in. Working solutions were prepared by the dilution of a standard solution with doubly distilled water. All containers, vessels and cells were washed with nitric acid (1:1) and doubly distilled water before use.

2.2. The instrumentation

The stripping analyzer M1 produced by Elektrouniverzal, Leskovac and the Faculty of Technology, Novi Sad, is a highly automated instrument for the potentiometric and chronopotentiometric stripping analysis with microprocessor control of the complete process. The analyzer has a program for automatic qualitative and quantitative analyses, including the calculation of element content. The electrochemical cell consists of a process vessel, an electromagnetic valve, a Teflon mechanical stirrer (1000–6000 rpm) and a three-electrode system. A glassy carbon (SIGRADUR-G) working electrode with 7.07 mm^2 total surface area was pressed into a Teflon tube (outer diameter 8 mm) at an elevated temperature. An Ag/AgCl, KCl (3.5 mol/L) electrode was used as the reference electrode and a platinum wire was used as a counter electrode [35].

A glassy carbon disc working electrode was used as inert support for the mercury film. Before the electrode formation, the glassy carbon surface was swept with filter paper first soaked in acetone and then in doubly distilled water. The mercury film was formed electrolytically from a solution containing 100 mg/L mercury (II)-ions and 0.02 mol/L hydrochloric acid, at a constant current of 50 μA for 240 s. Once deposited, the mercury film could be used for 25-30 analyses [36].

2.2.1. General Conditions of the PSA of Zinc, cadmium and lead

Here the PSA modification with oxygen as an oxidant was applied with the diffusion conditions of the mass transfer during the analytical step. This PSA modification is the simplest since it uses an already present diluted oxygen as a means of oxidation that reduces the contamination risk by applying other oxidation means.

For the PSA, it is necessary that the analyzed sample be in soluble form, and the pH value must be in within the range from 3.6 to 4.2. The parameters for the PSA determination of Zn, Cd and Pb in acid solutions, are shown in Table 1.

Table 1. The experimental conditions for the determination of Zn, Cd and Pb values by means of the PSA

Experimental conditions	
Deposition potential (Ag/AgCl /KCl 3.5mol/L) (V)	-1.498
Final potential (Ag/AgCl /KCl 3.5mol/L) (V)	-0.1
Deposition time (s)	600
Sample volume (L)	0.025
Resting time (s)	15
Stirring rate (rpm)	4000

The calibration curve method was used for zinc, cadmium and lead determination in acid solutions of analyzed samples (tobacco leaves, soil and cigarettes). For each sample five replicates were performed.

2.3. The samples

Three tobacco cultivars were used as samples in the research: Virginia, Burley and Oriental, gathered from 10 different sites (5 near industrial areas and major roads and 5 in rural areas), all grown in southeastern Serbia. The tobacco leaf samples were collected from a rural surrounding during the period between 2009 and 2010 year, with 30 samples collected per year (n = 60).

The total content of Zn, Cd and Pb was determined in the filler tobacco of 10 different brands of filter cigarettes, 5 from popular and 5 from fine brands of cigarettes (n = 10), which were purchased from the local market for purposes of comparison.

The content of these metals was also determined in the ash that remains after smoking cigarettes, which are analyzed in this paper.

Surface soil samples for heavy metal analyses were taken with a stainless steel auger, and were collected from the same locations at the same time as the tobacco samples (n = 20).

2.3.1. The preparation of the samples of tobacco leaf and filler tobacco of the cigarettes for the determination of total metal content

The analyzed samples (tobacco leaves and filler tobacco from the cigarettes) were measured after homogenization and treated with a mixture of concentrated HNO_3 and HCl in a ratio of 1:1.5

(V:V), heated at a temperature of 60-80 °C for 2 hours, in order to achieve their complete breakdown. After that, the samples were diluted, heated, filtered and stored in polyethylene bottles and analyzed [37, 38].

The ash that remains after the cigarette smoking, was dilluted in the mixture of concentrate acid according to regulation mention above.

2.3.2. The preparation of soil samples for the determination of total metal content

All of the soil samples were spread on plastic trays in fume cupboards and allowed to dry at ambient temperature for 8 days. The total amounts of Zn, Cd and Pb were determined by the digestion of the samples using HNO_3–HCl (aqua regia) by means of the conventional wet acid digestion method [39].

3. RESULTS AND DISCUSSION

First of all we checked the linearity and the reproducibility of the PSA analytical signal (τ_{ox} (s)) of zinc, cadmium and lead in solution. The analytical signal was found to be a linear function of zinc concentration within the range of 10–60 μg/L. The dependence of the PSA analytical signal (τ_{ox} (s)) on the mass concentration (C_{Zn}) follows the equation

$$\tau_{Ox}=0.0372+0.01744C_{Zn} \quad (1)$$

The analytical signals were found to be the linear function of cadmium and lead concentration within the range of 10–50 μg/L. The dependence of the PSA analytical signal (τ_{ox} (s)) on the mass concentration (C_{Cd}) follows the equation

$$\tau_{Ox}=0.098+0.0172C_{Cd} \quad (2)$$

and for lead (C_{Pb}) follows the equation

$$\tau_{Ox}=0.2232+0.01008C_{Pb} \quad (3)$$

According to the high values of correlation coefficients (r=0.99339 for zinc, r=1 for cadmium and r=0.99675 for lead) we concluded that there was a very good linearity of PSA analytical signals within the examined zinc, cadmium and lead concentration range.

Equations (1), (2) and (3) were used for calculation of Zn, Cd and Pb content in analyzed samples.

The total content of Zn, Cd and Pb in the tobacco leaf of the Virginia, Burley and Oriental cultivars, as in the soil at the given locations, are shown in Tables 2, 3 and 4, respectively. In Table 5 are shown the results for total metal content in the analyzed filler tobacco in the ash of cigarettes.

Table 2. The total content of Zn, Cd and Pb in the leaves of the Virginia tobacco cultivar and in the soil samples

	Samples											
	Tobacco leaves						**Soil**					
	C_{Zn} (µg/g)*	RSD (%)	C_{Cd} (µg/g)*	RSD (%)	C_{Pb} (µg/g)*	RSD (%)	C_{Zn} (µg/g)*	RSD (%)	C_{Cd} (µg/g)*	RSD (%)	C_{Pb} (µg/g)*	**RSD (%)**
Loc. 1	290.70	1.79	20.17	5.75	72.08	2.93	924.64	1.64	55.27	5.92	248.11	2.89
Loc. 2	274.40	2.67	19.97	6.11	64.01	1.80	1008.02	2.19	49.61	4.41	264.20	2.09
Loc. 3	266.32	1.80	19.55	6.65	58.95	4.02	956.11	1.83	62.36	6.56	270.54	3.44
Loc. 4	258.14	3.14	18.95	5.91	56.74	5.50	1153.02	2.54	58.14	7.09	295.74	3.42
Loc. 5	250.72	3.09	18.75	5.81	52.09	4.17	881.61	1.56	67.86	4.57	230.93	1.78
Loc. 6	238.20	3.45	15.20	7.24	49.82	3.45	861.20	1.12	21.58	9.41	96.78	3.65
Loc. 7	219.86	1.88	15.80	8.10	47.73	5.26	729.52	1.08	24.76	8.93	105.41	7.33
Loc. 8	215.30	1.49	13.67	7.90	42.31	4.94	833.83	1.71	19.68	5.49	89.70	6.91
Loc. 9	212.81	3.17	12.17	8.30	38.02	2.89	908.70	2.11	23.17	8.76	115.97	6.82
Loc.10	206.37	1.62	11.52	7.73	36.40	5.66	747.74	1.25	20.06	7.43	92.65	4.71

* Values represent mean content of five replicates

Table 3. The total content of Zn, Cd and Pb in the leaves of the Burley tobacco cultivar and in the soil samples

	Samples											
	Tobacco leaves						Soil					
	C_{Zn} (µg/g)*	RSD (%)	C_{Cd} (µg/g)*	RSD (%)	C_{Pb} (µg/g)*	RSD (%)	C_{Zn} (µg/g)*	RSD (%)	C_{Cd} (µg/g)*	RSD (%)	C_{Pb} (µg/g)*	RSD (%)
Loc. 1	240.91	2.95	18.05	8.42	70.17	5.90	872.21	2.19	65.74	6.48	218.42	3.48
Loc. 2	227.42	4.08	15.64	8.50	74.04	8.33	1121.01	2.86	53.63	5.91	282.12	3.26
Loc. 3	225.82	4.92	18.82	9.46	68.12	4.55	972.72	2.79	59.04	3.52	244.81	2.36
Loc. 4	222.10	2.88	18.65	6.17	62.56	5.53	917.74	2.79	62.83	5.44	265.93	1.54
Loc. 5	206.88	3.69	17.19	6.57	50.42	8.05	1011.08	3.48	55.22	7.35	220.72	3.23
Loc. 6	190.33	4.69	15.48	6.20	50.03	6.38	722.29	2.40	23.85	8.43	118.54	5.48
Loc. 7	140.72	4.34	14.39	7.78	40.66	6.64	875.16	2.28	19.39	5.62	91.41	3.30
Loc. 8	136.70	4.00	13.89	7.85	39.86	5.32	851.70	1.84	18.77	5.91	99.12	5.22
Loc. 9	124.35	6.29	15.35	6.84	36.65	8.35	914.52	2.26	23.27	9.24	102.53	6.00
Loc. 10	120.56	5.14	14.00	8.50	25.69	8.80	759.51	2.01	18.25	6.19	94.02	5.46

* Values represent mean content of five replicates

Table 4. The total content of Zn, Cd and Pb in the leaves of the Oriental tobacco cultivar and in the soil samples

	Sample											
	Tobacco leaves						Soil					
	C_{Zn} (μg/g)*	RSD (%)	C_{Cd} (μg/g)*	RSD (%)	C_{Pb} (μg/g)*	RSD (%)	C_{Zn} (μg/g)*	RSD (%)	C_{Cd} (μg/g)*	RSD (%)	C_{Pb} (μg/g)*	RSD (%)
Loc. 1	150.21	4.71	20.17	6.23	72.08	4.94	924.64	1.98	20.17	10.25	248.11	3.41
Loc. 2	147.73	3.73	19.97	7.57	64.01	7.00	1008.02	1.64	19.97	11.65	264.20	5.91
Loc. 3	128.10	3.25	19.55	5.51	58.95	5.87	956.11	2.51	19.55	7.34	270.54	3.68
Loc. 4	127.54	5.66	18.95	5.21	56.74	4.49	1153.02	2.05	18.95	6.34	295.74	4.83
Loc. 5	121.31	3.85	18.75	7.94	52.09	6.19	881.61	2.64	18.75	11.62	230.93	3.23
Loc. 6	118.92	2.55	15.20	2.58	49.82	5.31	861.20	2.69	15.20	5.84	96.78	3.12
Loc. 7	81.97	6.49	15.8	3.54	47.73	5.80	729.52	2.30	15.80	9.45	105.41	4.29
Loc. 8	79.66	5.11	13.67	3.16	42.31	5.01	833.83	2.30	13.67	8.19	89.70	4.68
Loc. 9	67.72	4.36	12.17	4.43	38.02	4.71	908.70	2.15	12.17	10.81	115.97	5.23
Loc. 10	54.45	5.60	11.52	1.64	36.40	5.04	747.74	1.71	11.52	6.63	92.65	4.98

* Values represent mean content of five replicates

Table 5. The total content of Zn, Cd and Pb in the filler tobacco and content in ash of cigarettes

	C_{Zn} (μg/g)*				C_{Cd} (μg/g)*				C_{Pb} (μg/g)*			
	C_T^+	RSD (%)	$C_A^‡$	RSD (%)	C_T^+	RSD (%)	$C_A^‡$	RSD (%)	C_T^+	RSD (%)	$C_A^‡$	RSD (%)
Cig. 1	55.62	5.61	22.14	7.18	7.94	1.51	2.77	8.30	6.77	4.28	3.15	2.86
Cig. 2	50.71	8.05	20.69	5.46	5.36	1.12	2.03	6.90	5.97	2.51	2.74	1.82
Cig. 3	35.37	5.94	15.88	6.36	6.61	1.36	2.45	1.63	6.15	3.41	3.02	0.99
Cig. 4	39.48	3.27	19.12	6.64	5.27	1.14	2.21	4.52	6.01	2.00	2.97	0.34
Cig. 5	49.15	6.25	21.03	5.33	4.79	1.46	1.68	5.36	3.55	1.69	1.81	3.87
Cig. 6	30.75	7.15	13.52	7.84	2.04	1.47	0.38	2.63	2.15	1.40	1.06	4.72
Cig. 7	25.12	7.44	10.17	8.46	2.14	2.34	0.54	7.41	1.97	2.54	0.83	4.82
Cig. 8	17.81	5.95	9.68	7.54	1.58	3.80	0.26	3.85	3.21	0.62	1.49	3.36
Cig. 9	20.63	7.56	11.32	9.63	0.96	5.21	0.12	8.33	1.62	0.62	0.71	1.41
Cig. 10	29.51	7.22	14.74	7.94	1.11	2.70	0.29	10.34	1.27	1.57	0.55	1.82

* Values represent mean content of five replicates.

C_T^+ – Total content

$C_A^‡$ – Content in ash

The results of this study indicate that the content of zinc in all of the analyzed tobacco and soil samples was significantly higher than that of Pb and Cd. The differences in the content of the determined metals in the cited samples were expected, considering the fact that the compounds which are used during the cultivation of tobacco (pesticides and fertilizers) contain significant amounts of zinc, which contributes to its elevated contents both in the soil and in the plant. On the basis of the literature review, we can conclude that the application of fertilizers in agriculture leads to the accumulation of high contents of zinc in the soil, up to 1500 ppm, Table 6 [31].

Table 6. Agricultural Sources of Trace Element Contamination in Soils (ppm DW) [31]

Element	Sewage Sludges	Phosphate Fertilizers	Limestones	Nitrogen Fertilizers	Manure	Pesticides (%)
Cd	2-1500	0.1-170	0.04-0.1	0.05-8.5	0.3-0.8	—
Pb	50-3000	7-225	20-1250	2-1450	6.6-15 (3500)[a]	60
Zn	700-49000	50-1450	10-450	1-42	15-250	1.3-25

[a] Mainly ammonium sulfate

The additional potential sources of contamination of the soil by means of heavy metals, in addition to the applied agrochemical measures, can also be different pollutants of the environment. Thus, the most common sources of highly toxic metals, lead and cadmium include exhaust fumes from industrial facilities and motor vehicles, dumps and waste water [31, 40]. By analyzing the soil samples from all the locations (Loc. 1-10) in this study, we can determine the influence of the proximity of the pollutant on the content of heavy metal in the samples of the soil where the tobacco was cultivated. Thus, the overall content of Zn, Pb and Cd in the soil from the locations which were in the immediate vicinity of the cited pollutants (Loc. 1-5) was higher in comparison to the locations in non-polluted areas (Loc. 6-10) (Tables 2-4). The content of zinc from locations 1-5 ranged from 750 to 1150 ppm, of lead ranged from approximately 200 to 300 ppm and cadmium of approximately 50 to 70 ppm, while from locations 6-10 it was lower and ranged from approximately 720 to 940 ppm for Zn, 80 to 120 ppm for Pb, and approximately 16 to 25 ppm for Cd. The influence of the proximity of the pollutant on the heavy metal content in the soil was confirmed in the work of M. Jung [41].

The tobacco plant can absorb heavy metals through the leaf (by means of the treatment with various agrochemical solutions), from the air (under the influence of atmospheric conditions), but also from the soil in which it is cultivated [11]. The results from this study indicate that the influence of the soil on the heavy metal content in tobacco leaves depends on the site on which the plant was cultivated (Tables 2-4). Nevertheless, the heavy metal content in the tobacco leaves of various cultivars (Virginia, Burley and Oriental) cultivated in the same locations, was different. Thus the highest content of Zn, Pb and Cd was detected in the tobacco leaf of the Virginia cultivar, and the lowest in the Oriental cultivar of tobacco. The content of zinc in the Oriental cultivar was approximately two times, of lead was approximately 0.5 and of cadmium was approximately three times lower than in the Virginia tobacco cultivar. Researches of some authors have showed that Oriental tobacco cultivar contains the least amount of toxic metals [12, 42]. This difference in the metal content, according to the tobacco cultivar, can be a consequence of the complexity of the process through which the metal is introduced into the plant, which has been confirmed in the research of some authors [43-45].

On the basis of the obtained results, we can conclude that the content of zinc in the cigarettes (popular and fine brands of cigarettes), as well as in the tobacco leaves and soil samples, was higher in comparison to the content of Pb and Cd. (Table 5). In the fine brands of cigarettes (Cig. 6-10), the determined content of zinc (in total and in the ash content) was about 1.5 to 2 times lower than in the popular cigarette brands. The content of highly toxic metals, Pb and Cd, in filler tobacco ranged within the same limits, from 3.5 to 8 ppm for popular brands of cigarettes, and 1 to 3.5 ppm for fine brands of cigarettes. In regards to their content in the ash, the content of lead was higher than that of cadmium, by about 1.5 to 2 times, which is consistent with the results obtained by Galazyn-Sidorczuk et al. [46]. Based on the results in Table 5, it can be seen that the content of heavy metals in filler tobacco was higher in relation to their content in the ash, that remains after cigarette smoking. The difference in the content of metals shown that for about 30-40% of the total metal content remain in the ash, a residue or ingested during smoking, or is released into the atmosphere, which poses a potential risk to passive smokers.

4. CONCLUSION

Based on these results, it can be concluded that tobacco (*Nicotiana tabacum L.*) has the ability to accumulate zinc and toxic heavy metals, lead and cadmium. The content of these metals in tobacco is affected by the use of agrochemical measures (fertilizers, pesticides), and the distance of the plots on which tobacco is grown from industrial areas and major roads. Thus, the content of Zn, Cd and Pb in the analyzed tobacco samples and soil samples which were close to industrial plants and major roads was higher than the content in the tobacco and soil samples taken from rural areas.

The Oriental tobacco cultivar had the lowest content of the studied metals in comparison to the other two analyzed tobacco cultivars, Virginia and Burley, at all the locations it was sampled from.

The total content of zinc, lead and cadmium in the filler tobacco in popular brands of cigarettes, and in their ash, was higher than the one found in fine brands of cigarettes.

The results shown clearly indicate that potentiometric stripping analysis can be successfully applied for zinc, cadmium and lead determination in soil, tobacco leaves as well as in different plant species. Both the sensitivity and reproducibility of the PSA method for the analysis of total zinc, cadmium and lead were determined.

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