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HEAVY METALS IN TOBACCO

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Abstract: *Heavy metals in cigarettes were determined considering that the number of smokers of both sexes is growing. Besides air, water, food raw materials, foodstuff, dietary supplements, the human body can accumulate heavy metals from tobacco. Tobacco samples from Romanian and Ukrainian market were analyzed using inductively coupled plasma mass spectrometry (ICPMS). The results showed that the Romanian samples have lower content of heavy metal than the Ukrainian samples. Tolerable weekly intake of cadmium was over in the case of two samples for minimum and maximum consumption and in the case of three samples for maximum consumption.*

Key words: *tobacco, heavy metals, risk assesment, tolerable weekly intake.*

1. Introduction

It is estimated that the actual number of substances in tobacco varies between 2000 and 3000, half of them existing in tobacco and the remainder resulting from the conversion into chemical processes that occur from burning tobacco. Hundreds of additives to improve the taste, odor, flavor of different varieties of tobacco are added to these. Besides these substances carcinogen acting radioactive isotopes (Pb210, Po201, K30 etc.) have been found in tobacco. An important factor in heavy metal uptake is the soil composition. The chemical composition of soil, pH, the humus content influenced Pb and Cd accumulation in leaves [1], [2], [3]. These elements were captured mainly by tobacco plants from radioactive substances forming the environment fund. The humus content influenced Pb and Cd accumulation in [1]. Industrial emissions, phosphate fertilizers containing cadmium [2], [3], insecticides based on heavy metals or metallic compounds of cadmium, mercury, lead, arsenic constitutes a health hazard to the consumer [5], [6], [7].
Cigarette smoking and tobacco chewing are a major source of cadmium exposure [8], [9].
Cigarette smoke is a very dangerous source of poisoning with Cd for both active smokers and passive ones. To highlight the heavy metals content in cigarettes 14 varieties of cigarettes, both Romanian and Ukrainian market, were analyzed.

2. Matherials and methods

2.1 Materials

Tobacco samples are presented and coded in Table 1.

Table 1.
Codification of samples

Sample code	Sample cigarettes	Country of origin
1	Kent Nanotek Neo	Romania
2	Kent Nanotek	Ukraine
3	Kent 8	Romania
4	Kent Clik	Romania
5	Winston Blue	Romania
6	Winston Balanced Blue	Ukraine
7	Фэст	Ukraine
8	Mallboro RED	Romania
9	Malboro Gold	Romania
10	Monte Carlo RED	Ukraine
11	Pall Mall	Ukraine
12	Pall Mall 3TEK Charcoal Filter	Romania
13	L&M Red Label	Romania
14	L&M Tune Slims	Romania

2.2 Sample preparation

Sample preparation is carried out in accordance with the standard SR EN ISO 14082:2003, *Determination of trace elements by atomic absorption spectrometry after ashing.*
Moisture content of tobacco samples was determined by oven drying method.
Ash content for each sample was determined by ashing in the furnace Nabertherm P330. Dissolving of ash is carried out according to SR EN ISO 14082:2003.
Ash of cigarettes taken from each sample was dissolved in 5 ml of hydrochloric acid concentration of 6 mol / L, the acid is evaporated in a water bath, and the residue was dissolved in a volume of 10 ml of nitric acid 0.1 mol / l

2.3 Reagents

All solutions were prepared with reagent grade chemicals and ultra-pure water (18 *MΩ cm*). Nitric acid and hydrochloric acid were purchased from Sigma Aldrich.

2.4. Apparatus

The analysis of samples was performed with mass spectrometry inductively coupled plasma ICP-MS Agilent Technologies 7500 Series precisely to 10^{-12}

2.5 Calculation of results

Concentration (C) of the heavy metals in samples is expressed in μg/g sample and is calculated using the formula:

$$C = a \cdot \frac{V}{m} \qquad (1)$$

where:
a - concentration value measured by the device, [ppb];
V - volume of acid dissolving the sample [ml];
m - mass of sample mineralized, [g].

2.6 Assesment of risk

The Estimated Daily Intake (EH s) was calculated for heavy metals and compared with tolerable Daily Intake (TD / S). The data is based on the assumption that body weight is 60 kg:

$$EDI=(CxFDC)/BW \qquad (2)$$

where:
C - the concentration of contaminant (*μg/g*),
FDC - stand for tobbaco daily consumption (*g/d*)
BW - the body weight (*kg*) [10].
The current tolerable weekly intake (TWI) of 2.5 *μg/kg* body weight (*b.w.*) for cadmium is established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 2010, and the CONTAM Panel of European Food Safety Authority EFSA reassessed the TWI in 2011 and concluded that the TWI of 2.5 *μg/kg b.w.* is still appropriate.

2.6. Statistical analysis

All analyses were carried out in triplicates with replication. The mean and standard deviation of the data obtained were calculated. Principal component analysis (PCA) was used to aggregate variables obtained from the amount of heavy metals (corresponding to a daily consumption of minimum 10 and maximum 20 cigarettes per day) into a smaller number of orthogonal factors. Principal Component Analysis was carried out with the software Unscrambler X 10.1 (Camo, Norway).

3. Results and discussions

Samples were always analyzed in triplicates. Ash content and moisture of the samples is shown in Figure 1.

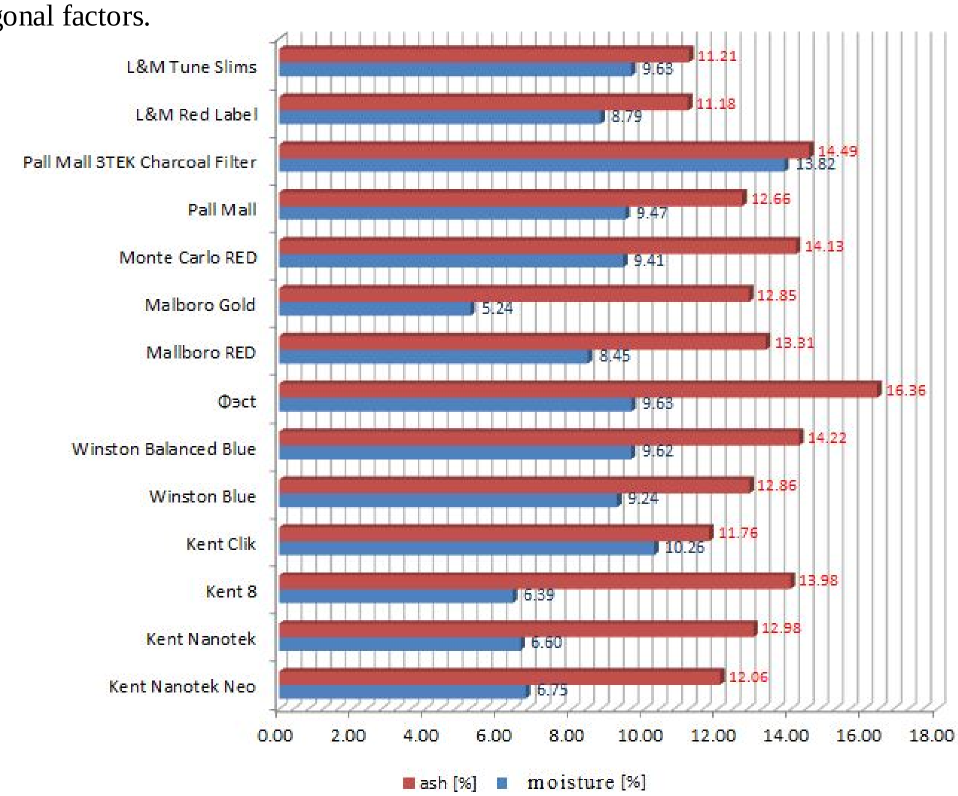

Fig. 1 Ash content and moisture of cigarettes samples

Heavy metal analysis was performed using ICP-MS device.

Taking into account the masses of samples and using equation (1), the amount of heavy metals corresponding to a daily consumption of minimum 10 and maximum 20 cigarettes per day was calculated [8].

As shown in Table 3, the content of the elements As, Pb, Hg is not exceeded even a consumption of 20 cigarettes per day, conclusions drawn also by other authors after analyzing a number of samples of tobacco [11-12].

Tabel 2

Elemental concentrations of samples

Sample	Kent Nanotek Neo RO 10/20 cigarettes [ppb]	Kent Nanotek RU 10/20 cigarettes [ppb]	Kent 8 10/20 cigarettes [ppb]	Kent Clik 10/20 cigarettes [ppb]	Winston Blue RO 10/20 cigarettes [ppb]	Winston Balanced Blue RU 10/20 cigarettes [ppb]	Фэст RU 10/20 cigarettes [ppb]	Mallboro RED 10/20 cigarettes [ppb]	Malboro Gold 10/20 cigarettes [ppb]	Monte Carlo RED RU 10/20 cigarettes [ppb]	Pall Mall RU 10/20 cigarettes [ppb]	Pall Mall 3TEK Charcoal Filter RO 10/20 cigarettes [ppb]	L&M Red Label 10/20 cigarettes [ppb]	L&M Tune Slims 10/20 cigarettes [ppb]
Li 7	12.98943 / 25.97887	11.72699 / 23.45398	14.38711 / 28.77422	11.13898 / 22.27796	15.36353 / 30.72706	13.79028 / 27.58055	9.93768 / 19.87535	11.00166 / 22.00332	6.65879 / 13.31757	17.11050/ 34.22100	3.63803/ 7.27606	10.91738/ 21.83477	18.31804/ 36.63608	9.25871/ 18.51742
B 11	14.17029 / 28.34058	7.94209/ 15.88418	7.81884/ 15.63767	8.14046/ 16.28093	10.88631/ 21.77261	8.71705/ 17.43409	5.93768/ 11.87535	6.33753/ 12.67505	5.96270/ 11.92540	8.20324/ 16.40649	16.65138/ 33.30276	4.80487/ 9.60973	13.17226/ 26.34452	3.16007/ 6.32014
Mg 24	2639.32049/ 5278.64098	2428.12823/ 4856.25646	2223.97476/ 4447.94953	2022.57439/ 4045.14879	1662.9682/ 3325.93656	1727.00644/ 3454.01289	2350.14164/ 4700.28329	1986.70781/ 3973.41562	1174.1528/ 2348.30575	2422.20182/ 4844.40363	2113.52288/ 4227.04576	1899.64521/ 3799.29042	1479.84667/ 2959.69334	1585.94211/ 3171.88423
Al 27	903.87404 / 1807.74808	1791.72699/ 3583.45398	750.67598/ 1501.35196	1124.50120/ 2249.00239	282.33912/ 564.67824	206.56122/ 413.12244	165.77904/ 331.55807	375.38571/ 750.77142	192.14605/ 384.29209	149.27048/ 298.54097	1219.09712/ 2438.19423	655.1444/ 1310.28890	471.94796/ 943.89592	378.47017/ 756.94034
K 39	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca 43	11412.8858 / 22825.77170	10566.7011/ 21133.40228	9361.19874/ 18722.3974	7763.08289/ 15526.1657	6929.9047/ 13859.8094	8329.23257/ 16658.4651	8962.03966/ 17924.07932	7843.57940/ 15687.1587	4083.2676/ 8166.53533	8783.79757/ 17567.59514	6327.32090/ 12654.64180	6699.44247/ 13398.88495	4772.91207/ 9545.82414	5772.29770/ 11544.59539
Cr 53	2.19598/ 4.39196	1.36505/ 2.73009	0.96890/ 1.93781	1.66458/ 3.32915	1.12257/ 2.24514	0.77329/ 1.54657	1.08782/ 2.17564	0.90197/ 1.80394	0.72235/ 1.44471	0.73462/ 1.46924	1.89544/ 3.79089	0.77040/ 1.54080	0.51109/ 1.02219	0.54637/ 1.09273
Mn 55	113.09302/ 226.18604	98.42813/ 196.85626	78.40243/ 156.80487	73.64041/ 147.28081	89.53139/ 179.06279	41.69889/ 83.39777	98.11898/ 196.23796	88.52362/ 177.04723	37.54925/ 75.09850	90.38874/ 180.77747	81.10670/ 162.21339	62.43284/ 124.86569	52.95621/ 105.91242	46.64796/ 93.29592
Fe 56	381.18914/ 762.37829	380.55843/ 761.11686	241.09959/ 482.19919	243.98586/ 487.97173	201.01814/ 402.03629	168.71705/ 337.43409	231.16147/ 462.32295	491.33634/ 982.67268	34.14762/ 68.29525	218.34507/ 436.69013	228.26862/ 456.53725	196.65484/ 393.30968	101.05703/ 202.11407	153.57354/ 307.14708
Co 59	0.87632/ 1.75264	0.79214/ 1.58428	1.51307/ 3.02614	0.59628/ 1.19257	0.53909/ 1.07819	0.49561/ 0.99121	0.66062/ 1.32125	0.58509/ 1.17019	0.26661/ 0.53323	0.68666/ 1.37333	0.55335/ 1.10670	0.57070/ 1.14141	0.44488/ 0.88977	0.44743/ 0.89486
Ni 60	3.02465/ 6.04931	1.98552/ 3.97104	3.67283/ 7.34565	1.77859/ 3.55718	1.90576/ 3.81151	1.47627/ 2.95255	1.88102/ 3.76204	1.49537/ 2.99074	0.99816/ 1.99632	2.10183/ 4.20365	1.89544/ 3.79089	1.78409/ 3.56817	0.99895/ 1.99791	1.12227/ 2.24454
Cu 63	15.26828/ 30.53657	11.72699/ 23.45398	9.88058/ 19.76115	9.88485/ 19.76970	12.23078/ 24.46156	7.69772/ 15.39543	17.41643/ 34.83286	7.91597/ 15.83195	24.12661/ 48.25322	16.70238/ 33.40475	6.89901/ 13.79802	4.73391/ 9.46782	4.72761/ 9.45522	5.27171/ 10.54341
Zn 66	24.03149/ 48.06298	19.85522/ 39.71044	17.57548/ 35.15097	16.64576/ 33.29153	15.14163/ 30.28325	11.24780/ 22.49561	17.67705/ 35.35411	17.32732/ 34.65464	11.29498/ 22.58997	13.87614/ 27.75227	14.87822/ 29.75645	12.77243/ 25.54486	9.98955/ 19.97909	9.30301/ 18.60602
Ga 69	3.70831/ 7.41661	3.08170/ 6.16339	0.85624/ 1.71248	1.24273/ 2.48546	1.13562/ 2.27124	0.38664/ 0.77329	0.30595/ 0.61190	0.59340/ 1.18680	0.19701/ 0.39401	0.27548/ 0.55096	0.65220/ 1.30439	1.51039/ 3.02078	0.25555/ 0.51109	0.75310/ 1.50620
As 75	0.60079/ 1.20157	0.49638/ 0.99276	0.63091/ 1.26183	0.51305/ 1.02611	0.36549/ 0.73098	0.60926/ 1.21851	0.70255/ 1.40510	0.65274/ 1.30548	0.28894/ 0.57788	0.78563/ 1.57127	0.59105/ 1.18211	0.49671 0.99341	0.34847/ 0.69695	0.36917/ 0.73833
Se 82	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br 79	22.58131/ 45.16263	14.68459/ 29.36918	8.90041/ 17.80081	13.56744/ 27.13488	10.44250/ 20.88500	16.28588/ 32.57176	13.48442/ 26.96884	7.35818/ 14.71635	1.97006/ 3.94011	6.12182/ 12.24365	8.15245/ 16.30490	9.02179/ 18.04359	3.02010/ 6.04019	3.54400/ 7.08801
Ag 107	60078.7238/ 120157.447	37228.5418/ 74457.0837	-	2280.2417/ 4560.48341	-	-	-	7120.8165/ 14241.6330	-	-	-	-	-	-
Cd 111	8701.05656/ 17402.1131	9720.78594/ 19441.5718	9689.0491/ 19378.0982	5472.5800/ 10945.1601	4568.5941/ 9137.1883	5858.2308/ 11716.4616	19943.3427/ 39886.6855	6883.4559/ 13766.9119	656.68505/ 1313.37011	10815.2229/ 21630.44587	7744.82829/ 15489.65658	3345.15966/ 6690.31931	3368.56778/ 6737.13556	-
Sn 118	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ce 140	191257.509/ 382515.019	205418.821/ 410837.642	168228.93/ 336457.863	136039.22/ 272078.440	155749.90/ 311499.804	71845.342/ 143690.685	93280.4532/ 186560.906	129741.27/ 259482.554	43761.491/ 87522.9839	73788.3889/ 147576.777	152165.494/ 304330.989	100679.168/ 201358.3375	71227.78488/ 142455.5697	65445.95393/ 130891.9078
Pt 195	0.00021/ 0.00041	0.00012/ 0.00025	0.00007/ 0.00014	0.00011/ 0.00023	0	0	0	0.000024/ 0.000047	0	0	0.00011/ 0.00022	0.000051/ 0.000101	0	0
Au 197	0.00056/ 0.00112	0.00141/ 0.00281	0.00025/ 0.00050	0.00025/ 0.00050	0.00035/ 0.00070	0.00009/ 0.00019	0.00008/ 0.00016	0.00017/ 0.00033	0.000066/ 0.000131	0.000031/ 0.000061	0.00036/ 0.00071	0.00002/ 0.00004	0.00028/ 0.00056	0.00028/ 0.00056
Hg 202	0.00601/ 0.01202	0.00786/ 0.01572	-	0.00160/ 0.00319	0.00026/ 0.00052	0.00269/ 0.00539	-	-	-	-	0.06950/ 0.13900	0.00030/ 0.00061	-	0.03869/ 0.07738
Pb 208	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bi 209	0.05652/ 0.11303	0.01030/ 0.02060	0.01947/ 0.03894	0.00727/ 0.01455	0.00559/ 0.01117	0.00408/ 0.00815	0.00519/ 0.01038	0.00330/ 0.00660	0.00234/ 0.00468	0.00253/ 0.00506	0.01455/ 0.02910	0.00373/ 0.00746	0.00451/ 0.00901	0.00174/ 0.00348
U 235	0.05179/ 0.10358	0.02482/ 0.04964	0.01915/ 0.03831	0.01938/ 0.03876	0.02741/ 0.05482	0.01640/ 0.03281	0.01700/ 0.03399	0.02492/ 0.04985	0.00867/ 0.01734	0.01530/ 0.03061	0.02446/ 0.04891	0.01723/ 0.03447	0.02672/ 0.05343	0.02215/ 0.04430

Per day levels were calculated considering a consumption of minimum 10 cigarettes and maximum 20 cigarettes

In contrast, the Cd content is exceeded in the case of three samples for a minimum consumption of 10 cigarettes per day, and the content is exceeded for five samples at a consumption of 20 cigarettes per day, figure 2.

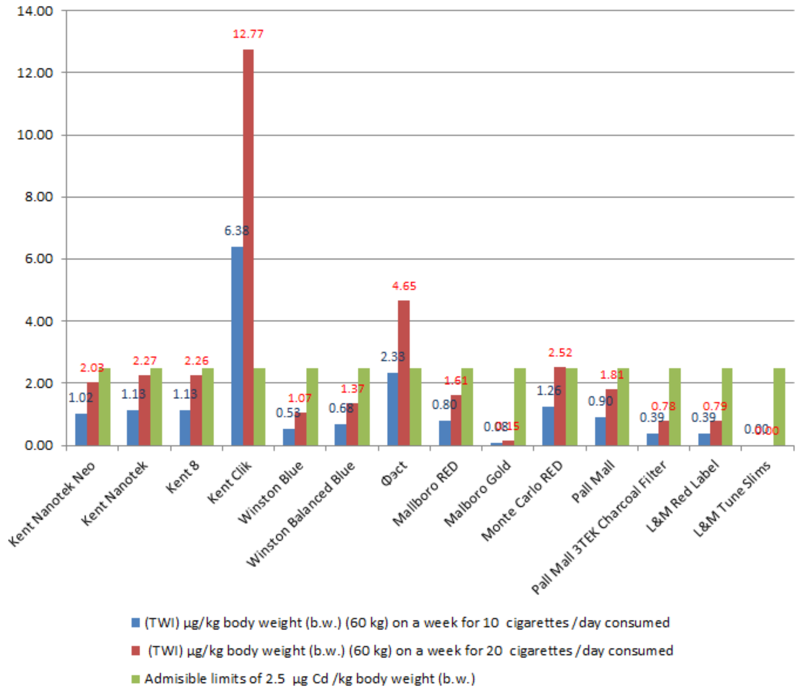

Fig. 2 Comparative analysis of the Cd content in Romanian and Ukrainian cigarettes

Principal Component Analysis was carried out according to the moisture content, ash and mineral concentrations in different samples of cigarettes. The scores of samples in the reduced space and the influence of chemical composition of the main component analysis are presented in figure 3 and figure 4.

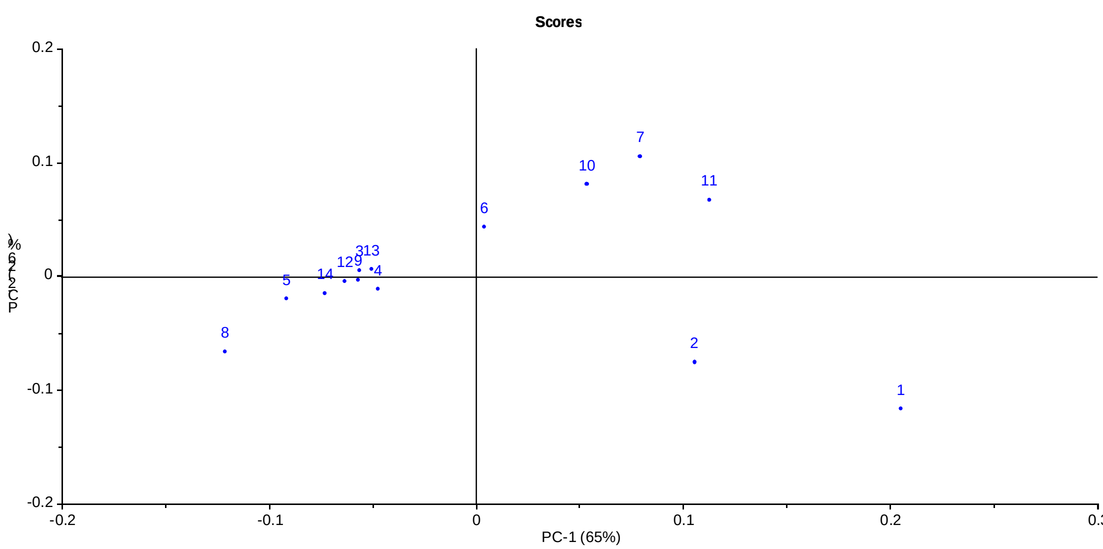

Fig. 3 Principal Component Analysis in different samples of cigarettes, according to the moisture and ash

This analysis identifies some kinds of cigarettes chemically similar. Principal Component Analysis was performed to assess the overall effect of chemical composition on the origin of cigarettes. Principal component 1 (PC1) explained 65% of variance, while component (PC2) explains 26% of variation, the overall percentage of variation of the two main components being 91% (figure 4).

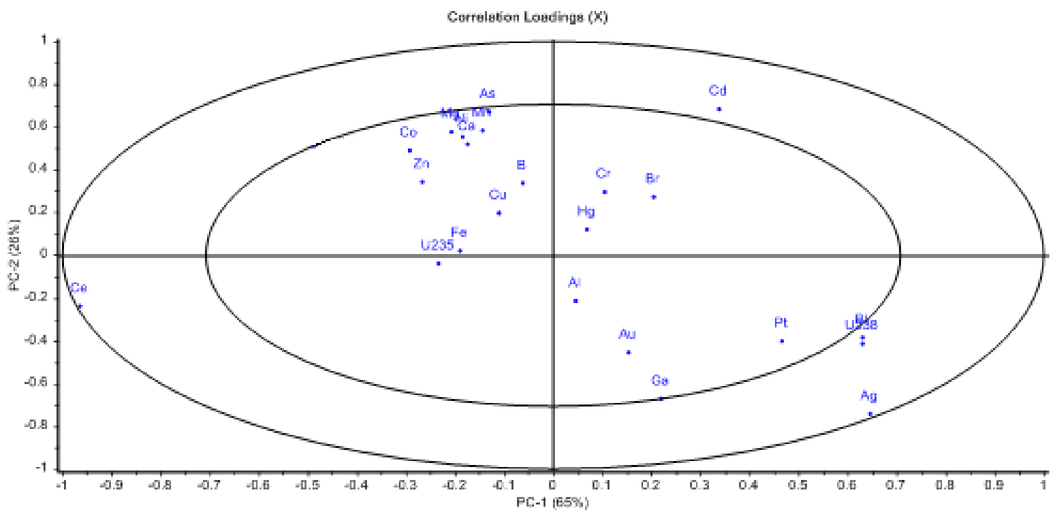

Fig. 4 Principal Component Analysis in different samples of cigarettes, according to the mineral concentrations

Component by PC1 distinguishes samples according to the content in Ag, Bi, U235 while PC2 component distinguished samples according to the content in As, Mn and Cd. The Hg and Al concentrations and proximity to the origin of the coordinates indicates that these parameters are not useful in the total variation. Component PC2 distinguishes types of cigarettes in two categories: on the left side there are Romanian cigarettes, while on the right side there are Ukrainian cigarettes. Cigarettes Kent Nanotek Neo Romania are in discordant note to the other Romanian cigarettes being placed close to the Ukrainian cigarettes because of metal content.

4. Conclusion

The metals Cu, Ni, Cr, Se, Hg, Pb were found to be neglijible. For cadmium, TWI was exceeded for Kent Clik cigarettes of 2.52 times, at a rate of 10 cigarettes per day, and of 5.10 times at a consumption of 20 cigarettes per day. In the case of Фэст cigarettes, TWI has been exceeded of 1.86 times at a consumption of 20 cigarettes per day. The penetration of toxic elements in the body is influenced by the moisture content of tobacco [9]. In the case of a high tobacco moisture more and more water vapor are generated which allows a drive of several toxic substances to the mouth end of the cigarette. Smoking of the last third of cigarette lead to increasing the ingestion of toxic substances from its total content determined.

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