2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-04-5

DETERMINATION OF As, Se AND Sb IN DIFFERENT TRADES AND BLENDS OF TOBACCO BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The concentrations of As, Se and Sb were determined in two different cigarette trades (M and F). For each trade, four blends were selected for analysis: red, blue, silver and gold for M and red, blue, silver and fresh for F. The As, Se and Sb concentrations were determined by neutron activation analysis. For the analysis the samples were dried to eliminate moisture and the results were given in dry weight. Samples were irradiated together reference standards materials in the IEA-R1 IPEN reactor and counted in Ge-hiperpure detector. It was observed that As and Sb showed higher concentrations in M than in F and no significant differences were observed between the blends.

1. INTRODUCTION

Nowadays 1.2 billion of smokers are spread around the world and 38 million in Brazil that is responsible for the majority of the worldwide exportation. *Nicotina tabacun* is the most important species which accounts for the majority of industrialized cigarette trade [1]. Brazil is the largest exporter of tobacco and 90% of the productions come from south region as well as the raw material used by the main cigarette producers Philip Morris and Souza Cruz [2,3].

The chemical composition of the tobacco depends on the plant which it derives, its provenance and growing method. The tobacco consumption is considered by WHO as the main cause of deaths by cancer. In Brazil the Agencia Nacional de Vigilância Sanitária (ANVISA) establishes mandatory regulations in order to determine the maximum amount of the main cigarette components and prohibits the use of definitions such as “ligh” that lead consumers to a misinterpretation about the levels contained in it since there are no legal safe limit for adverse effects [4]. Nicotine, carbon monoxide, ammonia, toluene, butane, tar and carcinogenic substances, polonium, benzene and toxic elements like lead, arsenic and selenium are among the more than 4700 toxic substances present in the tobacco. These substances are responsible for the threat in developing health problems such as cancer, coronary heart disease and pulmonary emphysema. Such substances are also released to the air, from the smoke cigar being a risk for non-smokers too [5,6].

The nonmetals arsenic, selenium and antimony are present in tobacco and, in spite of their biological functions, may represent a threat due to their high toxicological potential, mainly because all of them are considerably volatile. The objective of this paper is to determine the concentrations of As, Se and Sb in tobacco and the differences found among in their blends. It was chosen two of the most consumed trademarks and four blend of each one named F (red,

blue, silver and fresh) and M (red, blue, silver and gold). In addition other elements also determined by neutron activation analysis are presented to verify possible correlations with the elements of interest.

2. SAMPLING COLLECT AND PROCESSING METHOD

Samples were acquired in the regular commerce. Ten cigarettes were randomly chosen from the pack and the tobacco was separated from the paper and the filter, weighted, transferred to a mortar previously decontaminated with HNO_3 and left to dry in a furnace at 40º till constant weigh to moisture determination. Samples were than pulverized to 100 mesh, homogenized and approximately 200 mg were packed in polyethylene bags for irradiation.

Single synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No.41 filter paper and reference standard material Montana Soil (NIST 2710) were packed in the same way of the samples. In the IEA-R1 nuclear reactor at IPEN the samples, reference materials and synthetic standards were irradiated for 8 h and counted after 7 days to 15 days depending on the radionuclide half-live produced in the irradiation, under a thermal neutron flux of 1 to 5 x 10^{12} n cm^{-2} s^{-1}. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The data analysis were done by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations [7].

The concentrations were obtained by comparing the photopeak area of the interest element in the sample spectrum with that of the standard reference using the following expression:

$$C_{ai} = \frac{(A_{ai}\, w_p\, C_{pi})\, e^{-\lambda(ta - tp)}}{Ap_i\, w_a}$$

Were C_{ai} is the *i* element concentration in the sample (in mg kg^{-1}); C_{pi} is the *i* element concentration in the standard (in mg kg^{-1}); A_{ai} is the activity of the element *i* in the sample (in counts per second); A_{mi} is the activity of the element *i* in the standard (in counts per second); w_a e w_p are the weighs of the sample and standard (in g), respectively; λ is the element decay constant and t_a and t_p is the difference of the counting time between the sample and standard.

In table 1 are shown the determined elements and its concentrations in the reference materials used, the radioisotope formed during the irradiation, its half-life and the gamma energy used in its detection.

Table 1. Determined elements, concentration in the reference materials SRM-1571 and IAEA-336 in mg kg^{-1}, radioisotope formed during the irradiation, half-life and the gamma energy used in NAA.

Element	SRM-1571	IAEA -336	Radioisotope	E (keV)	Half-life
As	0.06±0.018	0.63±0.08	^{76}As	559	26.32h
Se	0.120±0.009	0.22±0.04	^{75}Se	246, 279.5	119.8d
Sb	NC	0.073±0.02	^{122}Sb	564-692	2.7d

The method precision and accuracy were verified by using the measurement of the standard reference material IAEA-336 (lichen).

3. RESULTS AND DISCUSSION

To verify the methodology samples of the reference material IAEA 336 (lichen) was analyzed and the results are shown in table 2 for the elements with certified values. The results indicate good precision and accuracy for the method.

Table 2: Measured (M) and certified (T), in mg kg^{-1}, values for reference material IAEA 336, n= 4.

	Br	**Ce**	**Co**	**Cr**
M	14±1	1.02±0.3	0.25±0.03	1.77±0.4
R	11.2-14.6	1.11-14.6	0.24-0.34	0.89-1.23
T	12.9	1.28	0.29	1.06
	Cs	**Eu**	**Fe(%)**	**La**
M	0.09±0.02	0.025±0.01	0.042±0.002	0.62±0.09
R	0.097-0.123	0.019-0.027	0.038-0.048	0.56-0.76
T	0.11	0.023	0.043	0.66
	Lu	**Rb**	**Sb**	**Sc**
M	0.006±0.002	1.75±0.2	0.09±0.05	0.17±0.02
R	0.0064-0.0068	1.54-1.98	0.06-0.08	0.15-0.19
T	0.007	1.76	0.07	0.17
	Se	**Sm**	**Tb**	**Th**
M	0.2±0.01	0.11±0.02	0.012±0.016	0.14±0.04
R	0.18-0.26	0.09-0.12	0.012-0.016	0.12-0.16
T	0.22	0.11	0.014	0.14
	Yb	**Zn**	**As**	**Sb**
M	0.085±0.02	25±5	0.6±0.2	0.05±0.01
R	0.025-0.049	27-33.8	0.55-0.71	0.063-0.083
T	0.037	30.4	0.63	0.073

M = measured value
R = reference material range of concentration
T = reference material true value of the element

Table 3 shows the results obtained in the moisture determination in the tobacco samples F (R, B, S and F) and in the tobacco samples M (R, B, S and F). The silver blend was the one that presented higher content of water and the blue blend lesser for both cigarette trademarks.

Table 3: Moisture content for the samples of F and M trades of cigarette.

Sample F	% of moisture	Sample M	% of moisture
FR	13.86	**MR**	15.33
FB	12.96	**MB**	13.18
FS	25.31	**MS**	25.11
FF	21.38	**MG**	19.18

Arsenic is a volatile element present in the tobacco leaves due to root uptake. This element is present in the particulate phase of cigarette smoke and may cause myocardial necrosis, and also has a carcinogenic effect [8]. Its more harmful form is the As^{+3} oxidation state due to its connection with the sulfhydryl group. Arsenic can also cause conjunctivitis, gastrointestinal and liver diseases, depigmentation and keratosis. It binds strongly to cells and is deposited in hair, nails and skin. The diary intake limit (DIL) for arsenic is 15 μg and the WHO recommend an As level of 10 μg L^{-1} for water ingestion [9]. In the present samples of tobacco, the concentration of As (table 4) is higher in the M trademark reaching values of 0.3 mg kg^{-1}. Considering a tobacco mean mass of 0.8g per cigarette, the consumption of one cigarette per day correspond to an ingestion of 0.24 μg of As assuming that all the arsenic present in the cigarette is ingested during the act of smoking.

Selenium is an essential nutrient for all the mammals. It has a fundamental importance in the human biology since it is involved in the metabolic process [10]. The DIL is restricted from 55 to 70 μg. On the other hand this element has a great toxic potential by ingestion and may cause several metabolic disorders such as in the kidneys, liver, brain and central nervous system. The risk of selenium ingestion is associated to the narrow range between the DIL and the toxic level. The cytotoxicity of selenium is dependent on the dose and related to the substances that can produce the anion selenide (RSe^{-}). The oxidative stress causes cell death by apoptosis or necrosis of tumor cells with greater possibility of occurrence in smokers than in non-smokers [11]. Considering the hypothesis stated above (that all the Se in the tobacco is transferred to the organism during the smoking) one cigarette consumed correspond to an intake of 2.4 μg of Se.

Antimony is a non-essential element for the humans and its toxicity depends on its oxidation state (the Sb^{+3} is more toxic than Sb^{+5}) and it is present in the cigar ash [12]. Besides the speciation the particle size, the antimony solubility and the individual age affect the amount of Sb absorbed. Once it reaches the bloodstream antimony accumulates primarily in liver to be distributed throughout the body, affecting mainly the lungs, intestines and kidneys. Antimony also has affinity for the spleen and blood and can cause irritation in the digestive mucosa, cardiotoxic effects, toxic hepatitis and hemorrhagic nephritis. The DIL for antimony is around 0,5 μg and the mean quantity of Sb found in the body is 2 μg generally associated to proteins as a substitute for sulfur atoms. The higher concentration of Sb was observed in the FB sample, but generally the trademark M possesses higher concentrations for this element.

If all the antimony present in the tobacco was transferred to the organism, the consumption of one cigarette corresponds to an intake of 0.12 μg of this element.

To verify the similarity between the trademarks and blends a cluster analysis was applied. The result is shown in figure 1. The blends G, B and R of the M trademark group together, another group was formed by the blends S, R and B of the F trademark together with the blend S of the M trademark. The sample FF was separated from the other samples probably because of its higher concentrations of Ce, La, Nd, Sm and Th.

Considering the elements presented in table 4, the M trademark possesses the general tendency of present higher concentrations for analyzed elements.

To establish the correlation between the elements of interest (As, Sb and Se) with the others also determined a cluster analysis was applied (figure 2). The arsenic presents good correlation mainly with the transition metals while Sb and Se show a correlation with Hf and Rb respectively.

4. CONCLUSIONS

Samples of four blends of two trademarks (named F and M) of the most consumed cigarettes were analyzed by neutron activation analysis and the concentrations of As, Sb and Se were determined. The M trademark presented higher concentrations for the elements studied as well as the other elements measured by the technique. It was verified that the consumption of these cigarettes contributes for the ingestion of As, Sb, and Se near or above the limits established for diary intake limit. It is also highlighted that there are no significant differences between the content of the analyzed elements in the different blend except for the blend Fresh (F) of the trademark F.

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Table 4: Results obtained for As, Sb , and Se analysis in tobacco samples, together with some other elements also determined by neutron activation analysis, in mg kg^{-1} except where indicated %.

	As		***Ba***		***Ce***		***Co***		***Cr***		***Cs***		***Eu***		***Fe(%)***		***Hf***		***La***	
MR	**0.2**	**±0.1**	123	±13	2.5	±0.2	2.01	±0.05	61	±3	0.27	±0.04	0.23	±0.06	0.118	±0.004	0.31	±0.02	1.6	±0.2
MB	**0.3**	**±0.1**	113	±12	3.2	±0.2	1.37	±0.04	20	±1	0.25	±0.04	0.28	±0.07	0.115	±0.003	0.27	±0.02	1.4	±0.2
MS	**<0.08**		96	±10	2.1	±0.2	1.33	±0.04	8.6	±0.5	0.17	±0.03	0.06	±0.01	0.102	±0.003	0.52	±0.02	1.6	±0.2
MG	**0.2**	**±0.1**	100	±11	3.0	±0.2	1.29	±0.04	11.6	±0.6	0.11	±0.03	0.27	±0.07	0.112	±0.003	0.24	±0.02	1.4	±0.2
FR	**<0.08**		85	±9	6.8	±0.2	0.80	±0.03	6.0	±0.4	0.10	±0.03	0.03	±0.00	0.067	±0.002	0.14	±0.01	1.4	±0.2
FB	**<0.08**		98	±9	1.9	±0.1	1.01	±0.02	12.2	±0.5	0.16	±0.02	0.03	±0.00	0.092	±0.002	0.57	±0.02	1.7	±0.1
FS	**<0.08**		89	±9	1.1	±0.1	0.73	±0.02	14.7	±0.7	0.08	±0.02	0.008	±0.004	0.052	±0.002	0.20	±0.01	0.7	±0.2
FF	**<0.08**		101	±11	15.3	±0.3	1.10	±0.03	47	±2	0.10	±0.03	0.21	±0.01	0.104	±0.003	0.35	±0.02	7.8	±0.4
	Nd		**Rb**		**Sb**		**Sc**		**Se**		**Sm**		**Th**		**Yb**		**Zn**			
MR	1.3	±0.4	24.0	±1.4	**0.06**	**±0.02**	0.310	±0.005	**3**	**±1**	0.33	±0.05	0.25	±0.02	0.04	±0.02	44	±2		
MB	1.0	±0.4	22.2	±1.3	**0.07**	**±0.02**	0.320	±0.006	**3**	**±1**	0.35	±0.05	0.36	±0.02	0.09	±0.02	40	±2		
MS	nd		22.8	±1.3	**0.05**	**±0.02**	0.310	±0.005	nd		0.34	±0.05	0.22	±0.02	0.07	±0.02	37	±2		
MG	1.2	±0.4	22.6	±1.3	**0.05**	**±0.01**	0.330	±0.005	**1**	**±1**	0.33	±0.05	0.39	±0.02	0.06	±0.02	42	±2		
FR	1.3	±0.6	20.6	±1.1	**<0.01**		0.170	±0.003	**3**	**±1**	0.21	±0.04	0.18	±0.02	ND		33	±1		
FB	1.0	±0.2	19.9	±0.8	**0.15**	**±0.03**	0.230	±0.003	**3**	**±1**	0.20	±0.02	0.32	±0.01	0.06	±0.01	37	±1		
FS	nd		17.8	±0.9	**<0.01**		0.140	±0.003	**2**	**±1**	0.14	±0.04	0.15	±0.02	0.09	±0.02	31	±1		
FF	6.3	±0.8	14.2	±0.9	**<0.01**		0.290	±0.004	**1.3**	**±0.5**	1.21	±0.05	0.99	±0.03	0.03	±0.01	35	±1		

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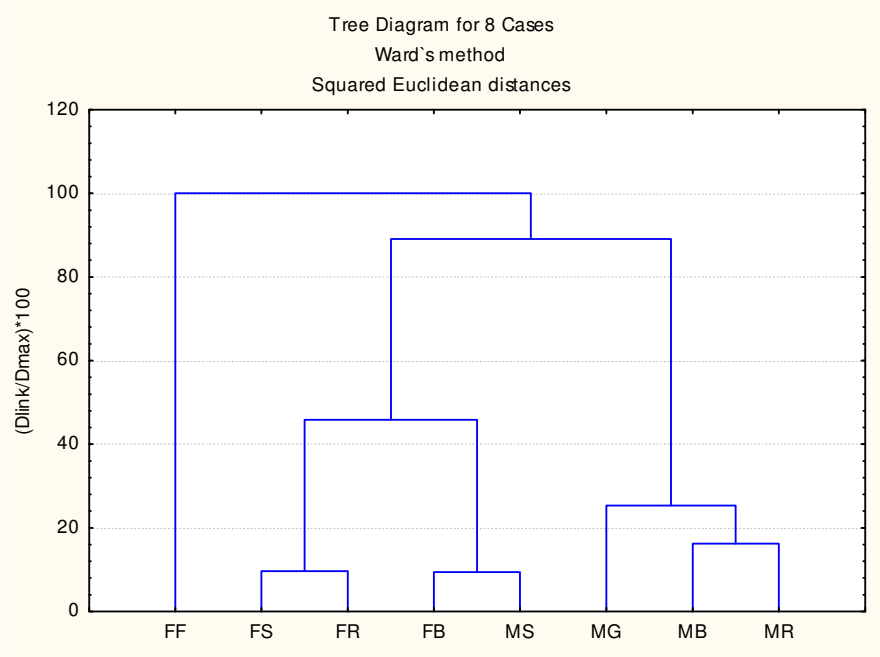

Figure 1: Dendrogram showing the similarity between the trademarks and blends.

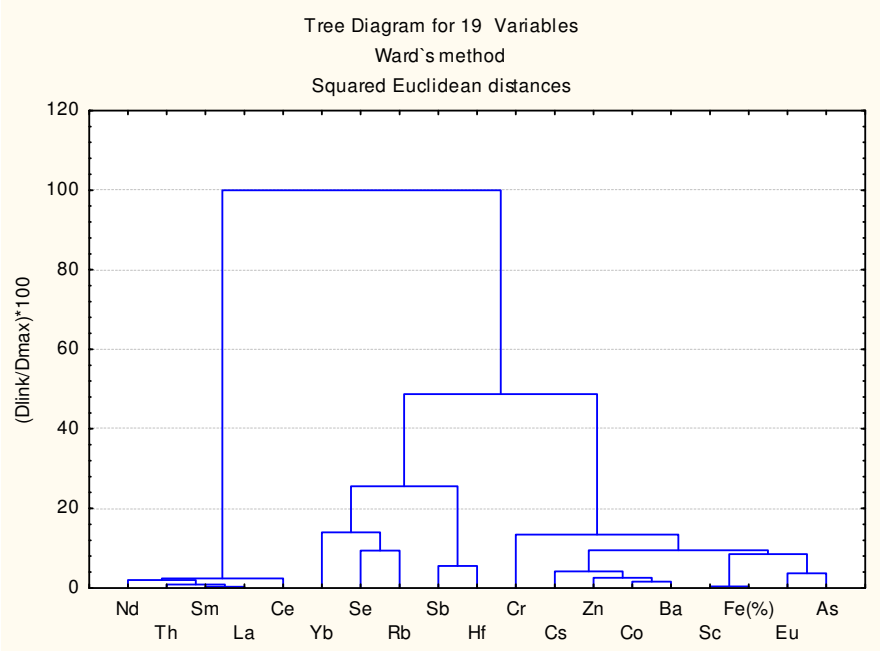

Figure 2: Dendrogram showing the similarity between the analyzed elements concentrations.

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