J.RADIOANAL.NUCL.CHEM.,LETTERS 108 /4/ 217-227 /1986/

DETERMINATION OF TRACE ELEMENTS IN BRAZILIAN CIGARETTE TOBACCO BY NEUTRON ACTIVATION ANALYSIS

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Received 28 December 1986
Accepted 8 January 1987

The determination of 14 trace elements /Ba, Ce, Co, Eu, Fe, Hf, La, Nd, Rb, Sb, Sc, Sm, Tb and Th/ has been carried out in three different brands of Brazilian cigarettes. The samples and standards were irradiated for 8 h at a thermal neutron flux of approx. 5×10^{12} n $cm^{-2} s^{-1}$. After the irradiation, the γ-rays activity was measured on a Ge/Li/ detector coupled with a 4096-channel pulse height analyzer. The results were compared with those obtained for the tobacco from American, Iranian, Turkish, Pakistan and Yugoslavian cigarettes. The amount of each element transferred to the ashes was determined.

INTRODUCTION

The tobacco plant is widely cultivated all over the world, thus indicating its adaptability to different soils and climates.

Elsevier Sequoia S. A., Lausanne
Akadémiai Kiadó, Budapest

The soil as well as the climate can be responsible for variations in the size, colour, width, length and thickness of the leaves and therefore in the distribution of the inorganic constituents which derives from the soil, the fertilizer and the specific agricultural technique used.

In the last years several papers concerning the analysis of trace elements in tobacco have been published[1-5]. Besides the organic elements considered carcinogenic, a great number of inorganic elements present in tobacco are suspected to be toxic[6].

It is therefore of interest to analyze the trace elements in tobacco of Brazilian cigarettes, considering the large smoking population, the different manufacturing processes and specially the variation in the microelements concentration in the soil and plants of different areas.

According to Leniham[7] and Leniham and Thomson[8] the elements, even in low concentrations, are so important in the biological activity processes that there are a relationship between several elements concentration in the body and the appearing of certain diseases.

In the present work, the instrumental neutron activation analysis was used to determine 14 elements in three different brands of Brazilian cigarettes chosen randomly and labelled as A, B and C.

For the choice of the three bands two different criteria were used: price and consumption. The A and C brands are those of higher and lower prices, respectively. The three analyzed brands were those of higher consumption within the same price.

Although the elemental concentration in the tobacco may give, by itself, information about the plant and its effects upon the smoke, it was considered convenient

to analyze the tobacco ashes and to determine the percent of transference.

Neutron activation analysis is adequate to this study since it provides a good sensitivity, selectivity and accuracy, as well as the possibility of a multielemental determination.

EXPERIMENTAL

Equipment

For the gamma-spectra measurement a solid state Ge/Li/ detector, ORTEC, model 8001-1022 V, No. 16-3911 was used. This γ-ray spectrometer was coupled to a 4096-multichannel analyzer, model 5410A Hewlett Packard.

The resolution of the system is 2.8 keV for the 1332 keV peak of ^{60}Co. The spectra analyses were carried out by using the FALA computer program[9] Once performed the peak identification, this program evaluates the corresponding area and its standard deviation by the Covel method[10]. The standard used was the AGV-1, provided by the U.S. Geological Survey. The elements concentration in this standard was compiled by Flanagan[11].

Irradiation and counting

The irradiations were carried out in the IAE-R1 reactor at "Commisão Nacional the Energia Nuclear - São Paulo" for 8 h at a thermal neutron flux of approximately 10^{12} n $cm^{-2}s^{-1}$.

Sample activities were measured 4 days after the irradiation to determine ^{153}Sm and ^{140}La. Countings

were repeated after approximately 15 days for the determination of ^{131}Ba and ^{147}Nd activities. Finally, the activity of the remaining radionuclides was measured after a decay time of about 30 days.

Experimental procedure

The samples were prepared by opening the cigarettes and rejecting the wrapping paper; the tobacco was then dried at 30 °C for 24 h. The tobacco was powdered in a quartz mortar to pass through a 100 mesh sieve and stored in glass containers.

Samples weighing approximately 100 mg were transferred to plastic ampoules of high purity for irradiation. The ampoules containing the sample and corresponding standard were wrapped in aluminium paper to avoid changes in their position during the irradiation.

The ash samples were obtained by calcinating the tobacco at 900 °C during 4 h in a platinum crucible.

Percent of transference /%T/

The percent of transference of the element from tobacco to the ashes was calculated by using the equation[12]

$$\%T = \frac{C_{ashes}}{C_{tobacco}} \times F \times 100$$

where

%T is the percent of transference, C is the element concentration in ppm and F is the weight of the ashes per gram of tobacco. For all the tobacco samples F was always equal to 0.11 g.

RESULTS AND DISCUSSION

The results for the contents of some trace elements /Ba, Ce, Co, Eu, Fe, Hf, La, Nd, Rb, Sb, Sc, Sm, Tb and Th/ in three different commercial brands available of Brazilian cigarettes tobacco are shown in Table 1. The concentration of Co is within the reported concentration range of the Turkish[12] and American[2] cigarettes. The Brazilian cigarettes are higher in Rb, Th, Eu, Ce, La and Sc concentrations when compared with Iranian[3] and Turkish cigarettes. The Sb concentration found, on the other hand, is much lower than the concentration present in the American cigarettes. For antimony, which is considered a highly toxic element, the concentration range found is similar to those reported for different brands commercially available in Pakistan[13].

The Rb contents in the Brazilian tobacco are almost the double of those found in the Iranian and Turkish tobacco. According to Tso[6] the Rb concentration is correlated with the plant size. Barium concentration found is higher than that of the Iranian tobacco, but very close to that of the Turkish tobacco. Barium is not considered an essential element for human beings.

The amount of Fe found in the Brazilian cigarettes is higher than that of Iranian, Turkish and American tobacco, though fall within the reported range of the Yugoslavian[14] brands. The high Fe concentration can be derived from contamination during the manufacturing process and from the use of pesticides.

From the range of the results it may be seen that the variation of trace elements in brands is relatively small. A statistical interpretation of the results was made in order to examine the differences observed

TABLE 1

Results for trace elements in tobacco of three different brands of Brazilian cigarettes /in ppm, unless % indicated/ and experimental F values

Brand	Ba	Ce	Co	Eu	Fe/%/	Hf	La
A	46.4	1.2	0.96	0.23	0.37	0.77	2.7
	45.8	2.8	0.73	0.27	0.34	0.87	3.1
	47.0	2.0	0.82	0.37	0.41	0.74	2.9
	47.6	1.9	0.90	0.32	0.33	0.82	2.6
Mean	46.7±0.8	2.0±0.7	0.85±0.1	0.30±0.5	0.36±0.04	0.80±0.06	2.8±0.2
B	54.3	3.9	0.73	0.040	0.087	0.19	2.7
	48.9	4.0	0.72	0.036	0.083	0.20	2.2
	52.1	3.9	0.75	0.047	0.087	0.17	2.8
	51.0	3.8	0.70	0.042	0.079	0.21	1.9
Mean	51.6±2.3	3.90±0.08	0.73±0.02	0.041±0.005	0.084±0.004	0.19±0.02	2.4±0.4
C	99.7	7.1	1.0	0.099	0.074	0.15	4.7
	98.7	7.5	1.0	0.106	0.071	0.16	4.8
	95.1	8.3	1.2	0.105	0.077	0.16	4.6
	96.3	8.1	1.1	0.099	0.076	0.15	4.7
Mean	97.5±2.1	7.8±0.6	1.08±0.09	0.102±0.004	0.075±0.003	0.160±0.006	4.70±0.08
Range	45.8-99.7	1.2-8.3	0.70-1.2	0.036-0.037	0.071-0.41	0.15-0.87	1.9-4.8
F_{exp}	927	140	19.3	57.7	244	438	4374

$F_{0.05/2.9/}=4.26$

Brand	Nd	Rb	Sb	Sc	Sm	Tb	Th
A	1.5	43.4	0.40	1.2	0.35	0.019	3.8
	1.2	44.1	0.30	1.5	0.29	0.028	3.6
	1.7	45.0	0.38	1.2	0.32	0.030	4.0
	1.4	42.0	0.28	1.4	0.28	0.021	3.2
Mean	1.5±0.2	43.6±1.3	0.34±0.06	1.3±0.2	0.31±0.03	0.025±0.005	3.7±0.3
B	2.5	30.9	0.084	0.24	0.26	0.030	0.35
	1.9	31.2	0.080	0.24	0.26	0.027	0.35
	2.3	34.2	0.079	0.25	0.24	0.031	0.36
	2.1	30.3	0.092	0.23	0.27	0.037	0.34
Mean	2.2±0.3	31.7±1.7	0.084±0.006	0.240±0.008	0.26±0.01	0.031±0.004	0.350±0.008
C	3.9	32.9	0.44	0.24	0.51	0.058	0.66
	4.2	32.4	0.47	0.24	0.52	0.059	0.66
	3.9	32.3	0.43	0.24	0.60	0.060	0.68
	3.8	30.8	0.47	0.23	0.57	0.057	0.84
Mean	4.0±0.2	32.1±0.9	0.45±0.02	0.240±0.005	0.55±0.04	0.059±0.001	0.71±0.09
Range	1.2-4.2	30.3-45.0	0.079-0.47	0.23-1.5	0.24-0.60	0.019-0.060	0.34-4.0
F_{exp}	269.3	101.4	109	208.9	98.6	82	316.3
$F_{0.05/2.9/}$	=4.26						

in the contents of each one of the elements analyzed, present in the three brands considered. As a criterion of comparison the F-test at a 0.05 significance level was applied.

The experimental F-values are listed in Table 1. All of them are higher than the tabulated F-value, 4.26, for 2 and 9 degrees of freedom at the 0.05 significance level. The hypothesis of equality of the samples analyzed must, therefore, be rejected.

By applying the F-test to the results obtained for the contents of each one of the 14 elements determined, it can be concluded that, as far as a particular element is concerned, at least one of the three brands is different from the other two. The F-test does not indicate, however, which brand is the different one.

For the purpose last mentioned the Scheffes[15] test was used, by applying the following equation:

$$\Delta = \left[MSr \left/ \frac{1}{n_{A_i}} + \frac{1}{n_{M_i}} \right/ \left/ n_C - 1 \right/ F_{2.9} \right]^{1/2}$$

where:

MSr - is the residual mean square,

n_C - is the number of columns /brands/,

n_{A_i} - is the number of lines /determinations/ for element i in brand A,

n_{M_i} - is the number of lines /determinations/ for element i in brand M /M=B or C/,

F - is the tabulated value: 4.26.

The contents of the elements in the samples of different brands were considered to be statistically the same, at a 0.05 significance level, when the differences between the mean values, $|\bar{X}_{A_i} - \bar{X}_{M_i}|$, obtained were equal to or smaller than Δ,

TABLE 2

Correlation coefficient for pairs of trace elements in tobacco

	Ba	Co	Fe	Sc	Hf	Eu	Sm	Nd	Tb
Ce	0.97							0.99	0.99
Eu	0.97		0.97	0.97					
La	0.97	0.99					0.99		0.95
Rb			0.99	0.99	0.99	0.98			
Sm	0.97	0.99							0.95
Th			0.99	0.99	0.99	0.99			

where

$\bar{X}_{A_i}$ - is the mean value of element i for brand A,

$\bar{X}_{M_i}$ - is the mean value of element i for brand M /M=B or C/.

For the values presented in Table 1 this condition is fulfilled for Rb, Eu, Th, Sc, Hf and Fe in brands B and C, and Co and Tb in brands A and B.

Table 2 shows the correlation coefficients calculated for pair of trace elements in tobacco; only the values which are statistically significant are given.

It can be observed that most of the elements exhibit a strong correlation. Such association may be due not only to the accumulation of the elements by soil contamination or the use of agricultural chemicals but also to some chemical compound added in throughout the cigarette manufacturing in order to improve the final product.

Table 3 presents the results concerning the transference percentage of each element from tobacco to the ashes.

TABLE 3

Transference percentage of some elements from tobacco to the cigarette ashes of three different brands /A, B and C

Element	%T		
	A	B	C
Ba	78.8	85.1	70.2
Ce	35.8	71.4	78.4
Co	69.4	84.0	58.0
Eu	37.0	56.3	67.1
Fe	77.3	83.1	90.9
Hf	89.9	71.2	69.2
La	74.3	83.8	64.1
Nd	68.9	92.5	68.2
Rb	19.0	25.2	31.6
Sb	24.2	61.9	35.9
Sc	57.5	96.0	78.0
Sm	86.4	81.2	78.0
Tb	84.6	99.0	81.2
Th	25.2	66.0	68.3

The transference of Co and Sb is of particular importance, considering the suspected toxic and tumerogenic properties of these elements.

It is important to note that only a small fraction of the majority of the elements analyzed is transferred into smoke.

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The authors wish to thank Dr. F.W. Lima and Dra L.T. Atalla for their encouragement throughout the work.

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