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DETERMINATION OF CHEMICAL ELEMENTS IN AFRICANIZED A*pis mellifera* (HYMENOPTERA: APIDAE) HONEY SAMPLES FROM THE STATE OF PIAUÍ, BRAZIL

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Honey is a food used since the most remote times, appreciated for its characteristic flavor, considerable nutritional value and medicinal properties; however, little information exists about the presence of chemical elements in it. The objectives of this work were to determine the chemical elements present in 38 honey samples, collected directly from beekeepers from the State of Piauí, Brazil and to verify whether they presented any contamination. The chemical elements were determined by means of Total Reflection X-ray Fluorescence. The means of three replicates were: K (109.671 ± 17.487), Ca (14.471 ± 3.8797), Ti (0.112 ± 0.07), Cr (0.196 ± 0.11), Mn (0.493 ± 0.103), Fe (1.722 ± 0.446), Co (0.038), Ni (0.728 ± 0.706), Cu (0.179 ± 0.0471), Zn (0.967 ± 0.653), Se (not detected), Br (not detected), Rb (0.371 ± 0.097), Sr (0.145 ± 0.45), Ba (11.681), Hg (not detected), and Pb (0.863) $\mu g\ g^{-1}$.

Keywords: honey; africanized honey bee; chemical elements.

INTRODUCTION

Different chemical elements are normally found in honey; however, at high rates they are considered pollutants. Honey can become contaminated with such pollutants by means of the air, soil, and water. Therefore, analyzing chemical elements in this product can provide information with regard to its quality as food or with respect to environmental pollution[1].

Accidental honey contamination comes from several sources, such as: residues of drugs used in bee disease treatment, which are administered orally, mixed with a sugar syrup and pesticide residues, particularly organochlorine and organophosphorus insecticides[2]. Landfills visited by bees can be sources of honey contamination by chemical pollutants.

Among the most dangerous pollutants, toxic chemical elements have been prioritized in studies. The most important are: cadmium, mercury, lead, copper, zinc, and nickel, which are present at low concentrations in the essential functions of living systems, but may become toxic when found above normal levels, depending on the type of organism exposed[3] . The same author has mentioned that a particular property of toxic chemical elements is that they are continually emitted from natural sources in the terrestrial and marine environments.

Tong *et al*.[4] reported that sources of air and water pollution by toxic chemical elements and other chemical elements include industries, mining, energy generation, and automobile exhaust. According to the above mentioned authors, mining pollution in a particular site may be limited to one or other chemical element, but contamination by industries or from energy generation includes a large number of toxic chemical elements or a combination of these. Intolerable limits of elements emitted from fuel oil or other urban traffic sources include: aluminum, calcium, copper, iron, lead, magnesium, silicon, barium, cadmium, chromium, nickel, palladium, platinum, and others which in certain regions are detrimental to health.

Toxic chemical elements form the only group of non-biodegradable environmental pollutants, reaching man by means of foods and consumption water. Although a fraction of the ingested amount is excreted, they possess a pronounced tendency for accumulation in man's vital organs, progressively exerting a toxic action for long periods, which also depends on their total accumulated dose, which in turn varies as a function of exposure time[5].

Scientific papers using bees and their products, including analysis of chemical elements in order to monitor environmental pollution have been developed in several countries. Since 1970, honey has been proposed as an environmental indicator for pollution evaluation in areas where hives are installed[6].

Brazil occupies an important position among honey producing countries, since it has a flora that is well suited for apiculture. However, information on the presence of minerals in honey composition is restricted. The State of Piauí, in the Northeast Region of Brazil, has gained projection in honey production, including organic honey producers. Thus, the present study was aimed at determining the concentrations of chemical elements present in *Apis mellifera* honey samples from the State of Piauí, in order to verify whether they present contamination.

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EXPERIMENTAL

Thirty-eight samples of honey produced by *Apis mellifera* L., 1758 (Hymenoptera: Apidae) were collected in the period from February to August 2002, directly from beekeepers of different municipalities in the State of Piauí (Pimenteiras 2 samples; Picos 35 samples; Socorro do Piauí 1 sample).

The analyses for honey chemical elements were carried out at the Apiculture Laboratory of "Departamento de Entomologia, Fitopatologia e Zoologia Agrícola of Escola Superior de Agricultura Luiz de Queiroz", Campus of "Universidade de São Paulo" (ash determination) and at the Nuclear Instrumentation Laboratory of "Centro de Energia Nuclear na Agricultura/Universidade de São Paulo", in Piracicaba, State of São Paulo, Brazil.

Initially, honey ash was obtained by burning approximately 10 g of the sample in a porcelain crucible by calcination in a muffle at 550 ^{o}C until constant weight; ash percentage was thus calculated[7].

The ash samples were submitted to wet digestion[8] in an open system using HNO_3/H_2O_2 (t = 130 ± 5 °C). After obtaining a clear solution, the volume was completed to 10 mL with deionized water. Ten µL Ga (internal standard, 1000 µg mL^{-1}) were added to a volume of 1 mL of this solution. A 20 µL aliquot was pipetted onto the center of a Lucite disc (3 cm in diameter) and dried under the action of infrared light. The samples were prepared with three replicates and detected in an X-ray spectrometer for 300 s.

Data analysis

The data were processed using SAS[9] ; the means (three replicates), confidence interval, and multivariate analysis were thus obtained.

Analysis of principal components was used to evaluate the importance of each chemical element studied on total available variation[10]. This technique is based on the standardization and rotation of orthogonal axes (chemical elements), generating a new set of coordinates (principal components) not correlated among themselves[11]. Highly correlated characters were discarded, using the criterion proposed by Joliffe[12], disregarding the variable with the highest coefficient in each component with an eigenvalue lower than 0.70.

The mean Euclidean distance and the UPGMA method (unweighted pair-group average) from the standardized data were used in the cluster analysis[13].

RESULTS AND DISCUSSION

The values corresponding to the chemical element concentrations analyzed in 38 samples of honey produced by *Apis mellifera*, from different municipalities in the State of Piauí are presented in Table 1 and the botanical origin of them, in the Table 2.

Most mean values for chemical elements obtained in honey samples from the State of Piauí conform to Brazilian law[14,15] (Tables 1 and 3). However, samples that do not conform to Brazilian law (samples nos. 4, 18, 24, 29, and 37) can be observed in Table 1.

In the present study, a variation from 0.038 to 0.412 µg g^{-1} was verified for the element Cr, and it was observed that 13.15% of samples (samples numbers. 4, 18, 24, 29, and 37) are above the established value, since Brazilian law has set a maximum value of 0.10 µg g^{-1}. Morse and Lisk[16] analyzed honey samples from several different countries and verified Cr values ranging from 0.843 to 2.67 µg g^{-1}; Caroli *et al.*[6,17], on the other hand, found in Italian honeys, values between 1.03 and 3.93 µg g^{-1}, which are well above those found in the present study.

For element Ni, a value of 7.19 µg g^{-1} was verified in one sample (sample number 24) (2.63% over the total), which is therefore above the maximum allowed by law, 5 µg g^{-1} at most. A maximum value of 7 µg g^{-1} was verified by Kump *et al.*[18] in Slovenia honeys, similarly to the value verified in the present study.

The high Cr, Ni, and Pb concentrations in the analyzed samples may indicate a possible environmental contamination according to papers by Tong *et al.*[4] in U.S.A., Merin *et al.*[19] in Israel and Braziewiez *et al.*[20] in Poland. According to Morse and Lisk[16], the presence of high contents of Cd, Cr, Co, Fe, Ni, Zn, and Pb in honey samples of several nations, may have as their source a galvanized steel container used in the processing and storage of this product. Tong *et al.*[4] observed that the U.S.A. honeys that came into contact with metal containers during processing showed high zinc contents.

Cu was found at a mean value of 0.179 µg g^{-1} (0.007 to 0.908 µg g^{-1}). The value established by Brazilian law for this element is 10.00 µg g^{-1} maximum; thus, all samples analyzed are in conformity with the law. Values near those in the present study were verified by Marchini *et al.*[21] in honey samples from the State of São Paulo; that author obtained values from 0.1 to 2.0 µg g^{-1} for wild flower honey samples. In turn, Nanda *et al.*[22] worked with honey of different floral sources from India, and verified Cu values ranging from 1.74 to 2.9 µg g^{-1}, well above those in the present study.

The following values were obtained for the chemical elements K, Ca, Ti, Mn, Fe, Co, Br, Rb, Sr, Ba, and Hg, which are not covered by Brazilian law: K was the chemical element with the highest amount as compared with other elements. The mean value found was 109.671 µg g^{-1}, varying from 2.180 to 204.77 µg g^{-1}. Yilmaz and Yavuz[23] analyzed honey samples from Turkey and observed a mean value of 296 µg g^{-1} for K, while Nanda *et al.*[22] verified values varying from 489.52 to 932.56 µg g^{-1} in Indian honey, well above those observed in the Piauí samples.

An average of 14.471 µg g^{-1} (0.385 to 76.759 µg g^{-1}) was observed for element Ca, which ranked second in amount. Marchini *et al.*[21] found higher values in honey from the State of São Paulo; Ca values varied from 55 to 301 µg g^{-1} for *Eucalyptus* flower honey, and from 1 to 202 µg g^{-1} for wild flower honey.

Element Ti was verified in 8 of the samples analyzed (3, 5, 14, 24, 25, 26, 28, and 29) and a mean value of 0.112 µg g^{-1} was observed (0.007 to 0.266 µg g^{-1}). Tong *et al.*[4] analyzed U.S.A. honey samples collected near mines, industries and highways, and verified Ti values ranging from 0.04 to 3.1 µg g^{-1}; therefore, they obtained values well above those observed in the present study.

The mean amount of element Mn was 0.493 µg g^{-1} (0.014 to 1.434 µg g^{-1}). Salinas *et al.*[24] analyzed honey samples from Spain and determined a mean Mn value of 0.8 µg g^{-1}; this mean is almost twice as high as that verified for the samples under study.

Fe had a mean value of 1.722 µg g^{-1} (0.067 to 7.053 µg g^{-1}). Marchini *et al.*[21] verified values varying from 2.1 to 9.0 µg g^{-1} in *Eucalyptus* flower honey samples from the State of São Paulo; these values were a little higher than those verified in the present work.

The element Co was verified in two samples (5.26%), with values of 0.037 µg g^{-1} (sample 14) and 0.039 µg g^{-1} (sample 24). A research developed by Morse and Lisk[16] with honey samples from different countries found Co values varying from 0.456 to 0.770 µg g^{-1}; these were therefore higher than those verified for Piauí samples.

The mean amount of Rb was 0.371 µg g^{-1} (0.007 to 1.528 µg g^{-1}). Iskander[25] verified Rb values varying from 0.88 to 0.97 µg g^{-1}, while Latorre *et al.*[26] analyzed honey samples from Spain and evidenced a mean value of 1.5 µg g^{-1}, near the upper limit of the amount observed in this work.

Sr was verified in 23 samples (60.52% from total), and a mean value of 0.145 µg g^{-1} (0.006 to 0.5370 µg g^{-1}) was observed; these values, however, were low when compared with those by Tong *et al.*[4], who found Sr values varying from 0.03 to 2.6 µg g^{-1} in U.S.A.

Table 1. Mean values (µg g^{-1}) of chemical elements in 38 samples of *Apis mellifera* honey from different municipalities of the State of Piauí, Brazil

Sample	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Se	Br	Rb	Sr	Ba	Hg
1	40.145	3.874	nd	nd	0.182	0.513	nd	0.021	0.055	0.206	nd	nd	0.230	nd	nd	nd
2	131.354	11.997	nd	nd	0.568	3.862	nd	nd	0.082	10.756	nd	nd	0.686	0.537	11.681	nd
3	159.004	18.775	0.266	nd	0.725	2.694	nd	nd	0.125	0.683	nd	nd	0.802	0.207	nd	nd
4	163.979	76.759	nd	0.110	0.865	1.394	nd	nd	0.241	0.487	nd	nd	0.589	0.108	nd	nd
5	144.347	21.208	0.242	nd	1.434	4.143	nd	nd	0.209	0.679	nd	nd	0.614	0.261	nd	nd
6	140.359	16.698	nd	nd	0.661	1.328	nd	nd	0.258	0.398	nd	nd	0.466	0.166	nd	nd
7	161.322	30.020	nd	nd	0.921	3.777	nd	0.144	0.311	0.663	nd	nd	0.471	0.219	nd	nd
8	58.209	12.425	nd	nd	0.388	0.728	nd	nd	0.130	3.907	nd	nd	0.218	0.134	nd	nd
9	123.960	10.949	nd	nd	0.331	1.169	nd	3.241	0.908	6.838	nd	nd	0.197	nd	nd	nd
10	174.743	18.663	nd	nd	0.766	4.636	nd	0.075	0.254	1.387	nd	nd	0.348	0.138	nd	nd
11	163.952	19.569	nd	nd	0.445	7.053	nd	nd	0.228	0.783	nd	nd	0.703	0.265	nd	nd
12	46.870	9.587	nd	nd	0.345	1.306	nd	nd	0.163	0.356	nd	nd	0.142	0.127	nd	nd
13	138.434	19.627	nd	nd	0.773	2.592	nd	nd	0.193	0.490	nd	nd	nd	nd	nd	nd
14	103.285	14.102	0.197	nd	0.371	2.003	0.037	0.021	0.183	0.241	nd	nd	0.385	0.110	nd	nd
15	123.649	15.680	nd	nd	0.685	2.468	nd	nd	0.336	0.634	nd	nd	0.648	0.182	nd	nd
16	152.359	17.278	nd	nd	0.613	1.568	nd	0.061	0.262	0.434	nd	nd	0.320	0.080	nd	nd
17	101.229	10.634	nd	nd	0.770	1.239	nd	0.021	0.062	0.192	nd	nd	0.332	0.057	nd	nd
18	128.453	18.959	nd	0.181	0.849	2.245	nd	0.163	0.244	0.348	nd	nd	0.303	nd	nd	nd
19	123.090	11.783	nd	nd	0.575	1.356	nd	0.038	0.107	0.681	nd	nd	0.310	0.117	nd	nd
20	87.802	9.684	nd	nd	0.317	1.019	nd	0.102	0.140	0.918	nd	nd	0.338	nd	nd	nd
21	50.543	6.658	nd	nd	0.212	0.677	nd	nd	0.078	0.171	nd	nd	0.109	nd	nd	nd
22	69.546	6.816	nd	0.038	0.160	0.536	nd	0.030	0.053	0.425	nd	nd	0.166	nd	nd	nd
23	82.259	13.219	nd	nd	0.471	0.931	nd	nd	0.133	0.395	nd	nd	0.303	nd	nd	nd
24	12.398	2.149	0.035	0.412	0.062	0.398	0.039	7.191	0.094	0.032	nd	nd	0.035	nd	nd	nd
25	21.237	3.361	0.058	nd	0.085	0.567	nd	0.337	0.041	0.069	nd	nd	0.094	0.032	nd	nd
26	8.862	1.687	0.028	nd	0.053	0.355	nd	0.006	0.029	0.085	nd	nd	0.034	0.026	nd	nd
27	204.777	22.212	nd	nd	1.318	1.954	nd	nd	0.104	0.801	nd	nd	0.427	nd	nd	nd
28	2.180	0.385	0.007	nd	0.014	0.067	nd	nd	0.007	0.010	nd	nd	0.007	0.006	nd	nd
29	31.736	4.309	0.061	0.114	0.151	0.846	nd	1.408	0.078	0.078	nd	nd	0.144	0.054	nd	nd
30	106.820	13.988	nd	nd	0.479	1.698	nd	0.122	0.257	0.391	nd	nd	0.185	nd	nd	nd
31	183.062	14.435	nd	nd	0.296	0.862	nd	nd	0.145	0.333	nd	nd	0.423	nd	nd	nd
32	203.133	19.678	nd	nd	0.467	2.027	nd	0.091	0.208	0.310	nd	nd	0.433	nd	nd	nd
33	113.789	9.567	nd	nd	0.258	1.427	nd	nd	0.070	0.326	nd	nd	0.313	nd	nd	nd
34	129.765	11.836	nd	nd	0.341	1.439	nd	0.102	0.269	nd	nd	nd	1.528	0.136	nd	nd
35	138.828	11.846	nd	nd	0.451	1.724	nd	0.026	0.160	0.358	nd	nd	0.456	0.136	nd	nd
36	132.732	13.036	nd	nd	0.618	0.875	nd	0.036	0.224	0.634	nd	nd	0.461	0.147	nd	nd
37	140.107	16.643	nd	0.322	0.399	1.313	nd	2.669	0.222	0.141	nd	nd	0.373	0.094	nd	nd
38	69.169	9.801	nd	nd	0.303	0.642	nd	0.112	0.125	0.127	nd	nd	0.147	nd	nd	nd

nd - not detected

honey samples near mines, industries, and highways.

Ba was verified in a single sample (sample no. 2) (2.63% from total) (11.681 µg g^{-1}). Lower values than those verified in this work were observed by Lasceve and Gonnet[27] (0.005 to 0.4 µg g^{-1}) in honey samples of France and Hungary.

Cluster analysis for chemical elements

In the principal components cluster analysis for 38 honey samples from the State of Piauí and for 14 chemical elements (Table 1), 12 were selected and 2 (Ni and Zn) were discarded, since they were highly correlated.

Variance estimate results (eigenvalues) are presented in Table 4.

From Table 4 it can be observed that the first component concentrated 30.75% of total variance, the second 47.90%, the third 62.32%, and the fourth 76.41%. It is noted that four principal components were required to explain 70% of total available variance among chemical elements, and thus considerable variance dispersion can be verified in the material studied.

Figure 1 show a phenogram prepared from the mean Euclidean distance and the UPGMA method, involving the 38 honey samples and chemical elements.

The criterion adopted to define groups was the linkage distances graph in the successive cluster analysis steps (Figure 2). This method is based on the identification of a plateau in the vertical direction, which means that many groups were formed at the same linkage distance; this distance is an optimal cutoff point on the phenogram and determines the number of groups formed. The cutoff point selected in this work was 18, represented by the horizontal line in Figure 1 and by the arrow in Figure 2.

From the phenogram (Figure 1) of samples studied, it can be observed that 9 groups were formed. Group 1 has 1 sample (Number 4); group 2 has 2 samples (Numbers. 32 and 27); group 3 has 2 samples (Numbers. 31 and 10); group 4 has 4 samples (Numbers 7, 16, 11, and 3); group 5 has 4 samples (Numbers. 33, 17, 30, and 14); group 6 has 12 samples (Numbers 35, 13, 37, 6, 5, 36, 34, 18,

Table 2. Botanical origin of 38 *Apis mellifera* honey samples from different municipalities in the State of Piauí, Brazil

Sample	Botanical origin	
	Scientific name	Popular name
1	*Mimosa verrucosa*	Jurema
2	*Mimosa verrucosa*	Jurema
3	*Piptadenia* sp.	Angico-de-bezerro
4	*Piptadenia* sp.	Angico-de-bezerro
5	*Piptadenia* sp.	Angico-de-bezerro
6	*Piptadenia* sp.	Angico-de-bezerro
7	*Piptadenia* sp.	Angico-de-bezerro
8	*Piptadenia* sp.	Angico-de-bezerro
9	*Mimosa caesalpineaefolia*	Sansão-do-campo
10	*Piptadenia* sp.	Angico-de-bezerro
11	*Mimosa caesalpineaefolia*	Sansão-do-campo
12	*Salvia* sp.+*Tibouchina* sp.+*Croton* sp.	Salvia + Quaresmeira + Marmeleiro
13	*Piptadenia* sp.	Angico-de-bezerro
14	*Piptadenia* sp.	Angico-de-bezerro
15	*Piptadenia* sp.	Angico-de-bezerro
16	*Piptadenia* sp.	Angico-de-bezerro
17	*Piptadenia* sp.	Angico-de-bezerro
18	*Piptadenia* sp.	Angico-de-bezerro
19	*Piptadenia* sp.+ *Borreria verticillata*	Angico-de-bezerro + Vassourinha-de-botão
20	*Mimosa verrucosa*	Jurema
21	*Piptadenia* sp.	Angico-de-bezerro
22	*Piptadenia* sp. +*Richardia* sp.	Angico-de-bezerro + Poaia
23	*Piptadenia* sp.	Angico-de-bezerro
24	*Piptadenia* sp.	Angico-de-bezerro
25	*Croton urucurana*	Sangra d'água
26	*Piptadenia* sp.	Angico-de-bezerro
27	*Piptadenia* sp.	Angico-de-bezerro
28	*Tibouchina* sp.+ *Mimosa caesalpineaefolia*	Quaresmeira + Sansão-do-campo
29	Polifloral	
30	*Piptadenia* sp.	Angico-de-bezerro
31	*Piptadenia* sp.	Angico-de-bezerro
32	*Piptadenia* sp.	Angico-de-bezerro
33	*Piptadenia* sp.	Angico-de-bezerro
34	*Piptadenia* sp.	Angico-de-bezerro
35	*Piptadenia* sp.	Angico-de-bezerro
36	*Piptadenia* sp.	Angico-de-bezerro
37	*Piptadenia* sp.	Angico-de-bezerro
38	*Piptadenia* sp.	Angico-de-bezerro

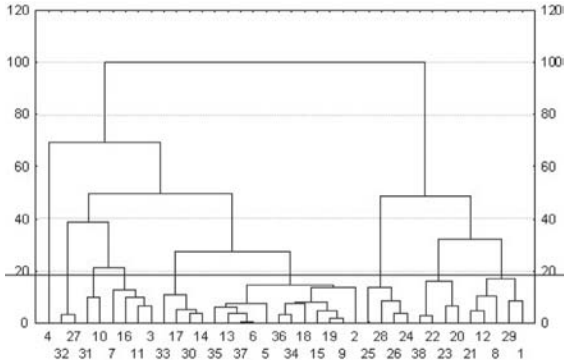

Figure 1. Phenogram obtained by cluster analysis, using mean Euclidean distance and the UPGMA method for 38 Apis mellifera *honey samples from the State of Piauí and 12 selected chemical elements*

Table 3. Values established by Brazilian law, mean value, confidence interval (5%), and minimum and maximum values for chemical elements found in 38 *Apis mellifera* honey samples from different municipalities in the State of Piauí, Brazil

Chemical Elements $\mu g\ g^{-1}$	Brazilian Law[14,15]	Mean	Minimum	Maximum
K	—	109.671±17.487	2.180	204.777
Ca	—	14.471±3.8797	0.385	76.759
Ti	—	0.112±0.07	0.007	0.266
Cr	< 0.10[15]	0.196±0.11	0.038	0.412
Mn	—	0.493±0.103	0.014	1.434
Fe	—	1.722±0.446	0.067	7.053
Co	—	0.038	0.037	0.039
Ni	< 5.00[15]	0.728±0.706	0.006	7.191
Cu	< 10.00[14]	0.179±0.0471	0.007	0.908
Zn	< 50.00[15]	0.967±0.653	0.010	10.756
Se	< 0.30[15]	nd	nd	nd
Br	—	nd	nd	nd
Rb	—	0.371±0.097	0.007	1.528
Sr	—	0.145±0.045	0.006	0.537
Ba	—	11.681*	—	—
Hg	—	nd	nd	nd

nd: not detected; * presence in only one sample

Table 4. Variance estimates (eigenvalues) and cumulative percentage of total variance (%) obtained by principal components analysis, considering 38 honey samples from Piauí, Brazil and 12 chemical elements

Principal components	Eigenvalues	% Accumulated
Y_1	4.3045	30.75
Y_2	2.4021	47.90
Y_3	2.0185	62.32
Y_4	1.9728	76.41

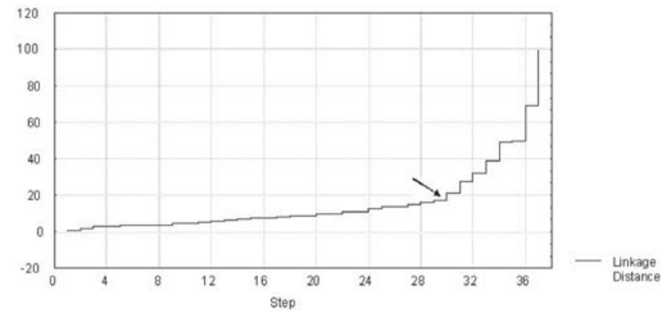

Figure 2. Linkage distance graph in successive clustering steps using the mean Euclidean distance and the UPGMA method. The arrow indicates the cutoff distance in the phenogram which defines groups in Figure 1

15, 19, 9, and 2); group 7 has 4 samples (Numbers. 25, 28, 26, and 24), group 8 has 4 samples (Numbers 38, 22, 23, and 20), and group 9 has 5 samples (Numbers 21, 12, 29, and 1).

Of the chemical elements analyzed for each axis (Table 5), those that contributed the most for the formation of groups on the X axis were Rb and K, and Hg and Ni on the Y axis.

By analyzing Table 1 and Figure 1 it is verified that a relation exists between groups and concentrations of element K. The groups

Table 5. Eigenvalues calculated for 38 honey samples from the State of Piauí, Brazil analyzed for chemical elements

Chemical elements	X Axis	Y Axis
K	**0.378539**	-0.016030
Ca	0.279348	-0.052895
Ti	0.096824	-0.036901
Cr	-0.172490	0.253550
Mn	0.362567	-0.095835
Fe	0.373555	0.026136
Co	-0.157498	0.217562
Ni	-0.208573	**0.462004**
Cu	0.145908	0.417868
Zn	0.200347	0.430989
Se	_____	_____
Br	_____	_____
Rb	**0.413225**	-0.020303
Sr	0.359073	0.110008
Ba	0.197784	0.223941
Hg	0.002136	**0.487461**
Pb	0.034531	0.013658

and K concentrations for the samples studied are distributed as follows: group 1 (163.97 μg g^{-1}); group 2 (203.13 to 204.77 μg g^{-1}); group 3 (174.74 to 183.06 μg g^{-1}); group 4 (152.3 to 163.95 μg g^{-1}); group 5 (101.22 to 113.78 μg g^{-1}); group 6 (123.09 to 144.34 μg g^{-1}); group 7 (2.18 to 21.23 μg g^{-1}); group 8 (69.16 to 87.80 μg g^{-1}), and group 9 (31.73 to 58.20 μg g^{-1}).

In honey, K is the chemical element found at the highest concentration. Crane[28] reported that honey contains more K than any other chemical element; this author also mentioned that the amount of K is 100 times higher than the amount of Fe.

CONCLUSION

Chemical elements with levels above those established by Brazilian law occurred in the analyzed samples for Cr (13.15% of samples) and Ni (2.63% of samples), thus disqualifying these samples.

Elements K, Rb, and Hg must be studied in more detail and included in the legislation, since they have great influence on product quality.

REFERENCES

1. Nobre, A. L. da R.; *Tese de Doutorado*, Universidade de São Paulo, Brasil, 1990.
2. Louveaux, J.; *Cahiers de Nutrition et de Diétetique* **1985**, *1*, 57.
3. Nürnberg, H. W.; *Pure Appl. Chem.* **1982**, *54*, 853.
4. Tong, S. S. C.; Morse, R. A.; Bache, C. A.; Lisk, D. J.; *Arch. Environ. Health* **1975**, *30*, 329.
5. Nürnberg, H. W.; *Analysis Chimie Acta* **1984**, *164*, 1.
6. Caroli, S.; Forte, G.; Lamiceli, A. L.; Galoppi, B.; *Talanta* **1999**, *50*, 327.
7. Pregnolato, W.; Pregnolato, N. P., coords.; *Normas analíticas do Instituto Adolfo Lutz*, 3ª ed., Instituto Adolfo Lutz: São Paulo, 1985.
8. Ward, A. F.; Marciello, L. F.; Carrara, L.; Luciano, V. J.; *Spectrosc. Lett*. **1980**, *13*, 803.
9. SAS Institute; *SAS/STAT: user's guide* – version 6. 4, Ed. Cary, 1990.
10. Mardia, L. V.; Keni, J. T.; Bibby, J. M.; *Multivariate analysis*, Academic Press: London, 1979.
11. Morrison, D. F.; *Multivariate statistical methods*, 2nd ed., Mc Grow Hill: Tokyo, 1981.
12. Joliffe, I. T.; *Applicant Statistical* **1973**, *21*, 21.
13. Cruz, C. D.; Regazzi, A. J. *Modelos biométricos aplicados ao melhoramento genético,* Universidade Federal de Viçosa: Viçosa, 1997.
14. http://e-legis.bvs.br/leisref/public/showAct.php?id=22, acessada em Agosto 2006.
15. http://e-legis.bvs.br/leisref/public/showAct.php?id=90#', acessada em Agosto 2006.
16. Morse, R. A.; Lisk, D. J.; *Am. Bee J*. **1980**, *120*, 522.
17. Caroli, S.; Forte, G.; Alessandrelli, M.; Cresti, R.; Spagnoli, M.; D'Ilioss, S.; Pouwels, J.; Kramer, G. N.; *Microchem. J*. **2000**, *67*, 227.
18. Kump, P.; Necemer, M.; Snajder, J.*; Spectrochim. Acta*, *Part B* **1996**, *51*, 499.
19. Merin, U.; Bernstein, S.; Rosenthal, I. A.; *Food Chem*. **1998**, *63*, 241.
20. Braziewiez, J.; Fijal, I.; Czyewski, T.; *Nucl. Instrum. Methods Phys. Res*., *Sect. A* **2002**, *487*, 231.
21. Marchini, L. C.; Moreti, A. C. C. C.; Otsuk, I. P.; *Ciênc. Tecnol. Aliment*. **2005**, *25*, 8.
22. Nanda, V.; Sarkar, B. C.; Sharma, H. K.; Bawa, A. S.; *J. Food Composition and Analysis* **2003**, *16*, 613.
23. Yilmaz, H.; Yavuz, O.; *Food Chem*. **1998**, *65*, 475.
24. Salinas, F.; Montero de Espanha, F.; Osório, E.; *Revista Espanhola de Ciencias y Tecnologia de Alimentos* **1994**, *34*, 441.
25. Iskander, F. Y.; *Sci. Total Environ*. **1996**, *192*, 119.
26. Latorre, M. J.; Peña, R.; Pita, C.; Botana, A.; García, S.; Herrero, C.; *Food Chem.* **1999**, *66*, 263.
27. Lasceve, G.; Gonnet, M.; *Apidologie* **1974**, *5*, 201.
28. Crane, E.; *Livro do mel***,** trad. de Astrid Kleinert Giovannini, Nobel: São Paulo, 1983.