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"Metals in Fresh Honeys from Tenerife Island, Spain"

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Abstract Ashes and contents of Zn, Cu, Fe, Cd and Pb in 140 fresh honey samples from three different areas of Tenerife Island were determined by inductively coupled plasma atomic emission spectrometry and graphite furnace atomic absorption spectrometry. A mean ash content of 0.35% has been determined. The mean Fe, Cu, Zn, Pb and Cd concentrations observed have been 3.37 mg kg^{-1}, 1.28 mg kg^{-1}, 2.83 mg kg^{-1}, 37.33 μg kg^{-1}, 4.38 μg kg^{-1}, respectively. A direct statistical correlation has been found between the Fe–Zn and Fe–Pb content, and between the Cd–Zn and Cd–Pb levels.

Keywords Essential metals · Toxic metals · Honey · Canary Islands

Honey is one of the oldest nutrient of humanity, an excellent indicator of pollution and it is useful for assessing the presence of environmental contaminants (Buldini et al. 2001; Przybytowski and Wilczynska 2001).

A recent paper about the mineral content in Canary Islands honeys determined major minerals in honeys from the seven islands (Hernández et al. 2005). In the present study, not only three essential metals (Fe, Cu and Zn) but the levels of two toxic metals (Pb and Cd) are used to characterized and evaluate the quality of Tenerife island's honeys.

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Fe, Cu and Zn are essential minerals for the human beings and diet is their main source (Rubio et al. 2004a, b). Heavy metals, like Cd and Pb, are considered as toxic environmental contaminants in foods (Rubio et al. 2004c, 2005). Trace element concentrations in honey samples from an industrial area are higher than in those from a relatively clean area.

Materials and Methods

Samples

A total of 140 samples of fresh honeys, not pasteurized neither subjected to any other thermal treatment gathered from three different areas in the island of Tenerife (South, North and Center) have been determined. All samples were supplied by House of the Honney that depends from an Official Institution ("Cabildo de Tenerife").

The plastic materials used for storing and treating the samples were cleaned using 5% nitric acid during 24 h followed with two washes with Milli-Q water.

Determination of Metals

Five grams of each sample were placed in porcelain crucibles and heated on a hot plate from 60°C to 80°C for at least 12 h. The crucibles with the samples were then introduced in muffle ovens and burned to ash at 450°C. The white ashes obtained with this procedure were then dissolved in 5% nitric acid to a volume of 50 mL.

The contents of Fe, Zn and Cu were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) with an ICP Thermo Jarrel Ash

Table 1 Instrumental conditions in the determination of Fe, Cu and Zn

Metal	λ (nm)	Power (w)	Argon flow (rpm)	Nebulizer flow (L/min)	Observation height (mm)	Slit height (mm)	Pump rate (s)
Fe*	259.940	1350	100	1	15	3	10
Cu*	324.754	1150	100	1	15	3	10
Zn*	213.856	1150	100	1	15	3	10

* Flow of the auxiliary gas: 1.0 L/min

rpm: revolutions per minute

Atom Scan 25 spectrometer. Cd and Pb determinations were done by a Perkin-Elmer spectrophotometer, model 4100 ZL Zeeman, equipped with a graphite furnace tube with an automatic sampler. In the lead and cadmium analyses, a mixture of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ were used as matrix modifiers. Table 1 presents the instrumental conditions during the determination of Fe, Cu and Zn and Table 2 displays the temperature program of the graphite furnace for Pb and Cd.

Quality control of the analytical measurements was performed using blank samples and the following reference material: NBS SRH 1515 apple leaves. The recovery obtained with the reference material were all above 98%.

Statistical Analysis

The statistical analysis of the obtained results consisted in a first Kolmogorov–Smirnov normality test and Shapiro–Wilk, followed by the study of the variance homogeneity using an ANOVA parametric test with a DMS post hoc and Tukey HSD test. Finally, in order to study a possible relation between the metals and the different geographical areas, a Pearson's correlations study was performed.

Results and Discussion

The median value and standard deviation contents of ashes, Fe, Cu, Zn, Pb, Cd are displayed in Table 3 by geographical areas. The median ash content in the North area is 0.48 ± 0.26%, being the ashes percentage in this area the highest value observed and significantly different from the ashes percentage observed for the other geographical areas.

For the Cd content, no significant differences have been observed among the different geographical areas. Honey from the North area presents the highest contents of Fe, Zn and Pb. Therefore, clear significant differences between the North honey and the other areas' honeys are observed. For Cu there are significant differences between the three areas of this study.

The Pearson's correlations results between content of metals show direct correlations between the Fe–Zn and Fe–Pb content and between the Zn–Cd and Cd–Pb concentrations.

Comparing the results of ashes with other authors, National data about Spanish honeys show an ash mean value of 0.192% (Rodríguez-Otero et al. 1992) for commercial honeys and 0.408% (Rodríguez-Otero et al. 1994) for honeys produced in Galicia.

Comparing the results of metals obtained by other authors (Table 4) it can be observed that levels of Fe and Zn that we have found are inferior to those found in commercial honeys. The copper concentrations in this study are similar to those previously reported. Fernández Torres et al. (2005) studied the mineral content of honeys from different places of Spain. The reported Cu concentrations are similar to ours but Zn levels are higher than the values we have obtained and the mean value for Zn in honeys from the Pomeranian region (Poland) is also much higher than the mean value for honeys from Tenerife. Fe levels in Turkish honeys double the mean value of Fe in Tenerife but Zn and Cu present very similar values.

In general, the concentrations of Pb and Cd are low and show the absence of contamination, a fact that is on the other hand logical, given the absence of industrial pollution in the sampling areas. These results are very similar to those found in Poland (Przybytowski and Wilczynska 2001).

If a mean consumption of 20 g of honey per person and day is considered for the Canarian population, the contribution of the daily intake of honey to the Recommended Dietary Allowances of Fe, Cu and Zn should be taken into account. The Fe, Cu and Zn RDAs for adults are: 8–11 mg Fe day^{-1} for men and 8–18 mg Fe day^{-1} for women; 700–900 µg Cu day^{-1} for men and

Table 2 Graphite furnace's temperature program in the determination of Cd and Pb

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow
Drying 1	110	1	20	250
Drying 2	130	5	30	250
Pre-treatment	800 (Cd) 850 (Pb)	10	20	250
Atomization	1500[a]	0	5	0
Clean out	2400	1	2	250

[a] Reading temperature

Matrix modifier: Mg $(NO_3)_2/NH_4H_2PO_4$

Wavelength for Pb: 217 nm

Wavelength for Cd: 228.8 nm

Injection volume for Pb: 25 µL

Injection volume for Cd: 15 µL

Injection temperature: 20°C

Table 3 Concentration of the analyzed elements and % of ashes (Median value ± Standard deviation)

Ashes (%)	Fe (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Pb (μg kg^{-1})	Cd (μg kg^{-1})
South					
0.25 ± 0.08	3.15 ± 1.26	1.22 ± 0.93	2.69 ± 1.43	31.50 ± 11.97	4.21 ± 2.34
North					
0.48 ± 0.26	4.70 ± 2.24	0.74 ± 0.53	3.47 ± 1.81	46.32 ± 20.90	4.56 ± 2.15
Center					
0.32 ± 0.08	2.26 ± 0.77	1.88 ± 0.53	2.34 ± 0.56	34.16 ± 9.16	4.38 ± 1.29

Table 4 Metal contents in honeys from different origins

Origin	Reference	Fe (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Pb (μg kg^{-1})	Cd (μg kg^{-1})
Spanish commercial honeys	Rodríguez-Otero et al. (1992)	5.3	0.62			
Galicia (Spain)	Rodríguez-Otero et al. (1994)	5.12	0.62			
Turkey (south-eastern Anatolia)	Yilmaz and Yavuz (1999)	6.6	1.8	2.7		
Poland Pomeranian region	Przybytowski and Wilczynska (2001)			7.76	48	15
Egypt (clover honey)	Rashed and Soltan (2004)				4200	10
Egypt (sesame honey)						500
Spanish honeys	Fernández Torres et al. (2005)		0.531–2.117	1.332–7.825		
Tenerife	This study	3.37	1.28	2.83	37.33	4.38

women and 8–11 mg Zn day^{-1} for men and 8–9 mg Zn day^{-1} for women (Institute of Medicine, Food and Nutrition Board 2001). Therefore, consuming 20 g per day of honey from Tenerife provides: 0.0674 mg Fe day^{-1}, what means between 0.84% and 0.61% for men and between 0.37% and 0.84% for women of the RDA; 0.0256 mg Cu day^{-1} (25.6 μg Cu day^{-1}), 2.84%–3.66% of the RDA; 0.0566 mg Zn, or between 0.51% and 0.71% for men and between 0.63 and 0.71 for women of the RDA. These results make us conclude that, although Cu is the metal with lowest concentration among the honeys that have been analyzed, it is the one which provides more to its RDA.

However, the contribution of a daily 20 g honey intake to the Provisional Tolerable Weekly Intakes (PTWIs) fixed by the WHO for Pb and Cd (WHO 1993) are irrelevant being 0.7466 μg Pb day^{-1} (5.2262 μg Pb $week^{-1}$) and 0.0876 μg Cd day^{-1} (0.6132 μg Cd $week^{-1}$). This represents, for an average person weighting 65 kg, approximately 0.322% of the PTWI in the case of Pb and 0.135 for Cd. Nevertheless, it should be taken into account that there are other sources of these metals to the diet.

In conclusion, the honey's ash contents are, in general, common to those attributed to honeys of floral origin. Fe, Cu and Zn concentration levels in Tenerife honeys are low. The mineral element which presents the highest level is Fe, followed by Zn and Cu. Cd and Pb levels are also very low. Since no specific legislation on honey's mineral content exists, if we were to compare our results to the maximum fixed in the legislation for other types of food, we would find that our values are very low. Finally, direct statistical correlations have been found between the Fe–Pb and Fe–Zn contents, and between the Cd–Zn and Cd–Pb levels.

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