Short Communication

Detection of Metals in Different Honey Brands

Ufuk Tansel ŞİRELİ [1] 🖉   Güzin İPLİKÇİOĞLU ÇİL [1]
Begüm YURDAKÖK DİKMEN [2]   Ayhan FİLAZİ [2]   Hüseyin ÜLKER [1]

[1] Ankara University, Faculty of Veterinary Medicine, Department of Food Hygiene and Technology, TR-06110 Dışkapı, Ankara - TURKEY
[2] Ankara University, Faculty of Veterinary Medicine, Department of Pharmacology and Toxicology TR-06110 Dışkapı, Ankara - TURKEY

Abstract

In this study, cadmium (Cd), lead (Pb), iron (Fe), zinc (Zn), aluminium (Al), mercury (Hg) and copper (Cu) levels determined in a total of 100 honey samples belonging to 15 different companies, by atomic absorption spectrometry. The mean values were found Cd 0.343, Pb 1.101, Fe 41.13, Zn 6.76, Al 1.490, Hg 0.618, Cu 0.06 mg/kg. These results showed that the metal levels were known to be within the acceptable limits so honey is safe for metals which are harmful for human health. This data also indicates that, honey production is made in accordance with the regulations and it's under control.

Keywords: Honey, Metal, Atomic absorption spectrometry, Environmental contamination

Farklı Marka Ballarda Metal Seviyelerinin Tespiti

Özet

Bu çalışmada, 15 farklı firmaya ait 100 adet bal numunesindeki kadmiyum (Cd), kurşun (Pb), demir (Fe), çinko (Zn), alüminyum (Al), civa (Hg) ve bakır (Cu) seviyeleri atomik absorbsiyon spekrometresi ile araştırılmış ve metallerin ortalama değerleri Cd 0.343, Pb 1.101, Fe 41.13, Zn 6.76, Al 1.490, Hg 0.618, Cu 0.06 mg/kg olacak şekilde saptanmıştır. Bu sonuçlar ballardaki metal miktarların kabul edilebilir seviyelerde olduğunu ve ülkemizde bal üretiminin yasal düzenlemelere uygun yapıldığını ve kontrol altında olduğunu da göstermektedir.

Anahtar sözcükler: Bal, Metal, Atomik absorbsiyon spektrometresi, Çevresel kontaminasyon

INTRODUCTION

Honey is a sweet, viscous substance mainly produced by honey bees *(Apis mellifera)* from nectar of different plant flowers and secretion of plants or plant-sucking insects [1]. In honey the main nutrition component is the carbohydrates, fructose and glucose which make it, an excellent energy source. Honey contains also a number of other constituents in small and trace amounts, producing numerous nutritional and biological effects: antimicrobial, antioxidant, antiviral, antiparasitic, antiinflammatory, anti-mutagenic, anticancer and immunosuppressive activities [2]. An important aspect of honey quality is the presence of contaminants due to environmental contamination or pharmacological (antiparasitical or acaricidal) residues [3]. One of the most concerned contaminant in honey is metals. Major metals are primarily derived from soil and nectar-producing plants [4]. Environmental pollution or other anthropogenic sources of metals in honey are also important for accumulation. Honey can also be contaminated with some transition metals during its processing through the equipment and tools used by the beekeepers long with the processing environment [5]. After prolonged evaluation studies on food additives and their toxicity, the World Health Organization (WHO) has concluded that even low levels of some metals, such as Pb and Cd, can cause several diseases in humans [6]. The objective of this study was to determine the levels of some metals, Cd, Pb, Fe, Zn, Al, Hg and Cu, which are considered among the most dangerous to human, in honeys from Turkey.

MATERIAL and METHODS

Samples

A total of 100 honey samples belonging to 15 different

🖉 İletişim (Correspondence)
☎ +90 312 3170315
✉ utsireli@ankara.edu.tr

companies were analyzed as an indicator of environmental contamination. 250 g of each sample was placed in a plastic bottle and kept in a dark, dry and clean place until the analysis.

Sample Preparation

Approximately 0.5 g honey was placed in a polytetra-fluoroethylene (PTFE) vessel and 10 ml of concentrated nitric acid (HNO_3) was added. The digestion was carried out with the following digestion program: 500 W 15 min up to 210°C; then 1050 W 15 min at 210°C. After cooling, the vessels were opened and 2 mL H_2O_2 was added to the digest and the same temperature program was repeated. The digests were made up to 25 mL using ultrapure water. Process blanks were also prepared in a similar manner.

Apparatus

Analytical grade reagents were used throughout the analysis. Metal concentrations in the honey were determined by using a continuum source graphite furnace atomic absorption spectrometer (CS-GFAAS) Model Contra AA 700 equipped with a transversely heated graphite tube atomizer and a MPE 60 autosampler (Analytik Jena AG, Jena, Germany). A xenon short arc lamp in hot-spot mode operated at 300 W was used as a continuum radiation source. A high-resolution double monochromator, consisting of a prism as pre-monochromator and an echelle grating monochromator, providing a spectral bandwidth *per*

pixel of *ca*. 2 pm at 200 nm, was used to promote spectral dispersion of the continuum radiation and a linear charge coupled device array detector with 588 pixels for the detection of the radiation. Argon with a purity of 99.99% was used as the purge gas with a flow rate of 2 L min^{-1} in all stages, except during atomization step. The samples were digested in high pressure 1500 Teflon vessels using a MARS (CEM, Matthews, NC, USA) microwave digester equipped with temperature and pressure sensors. In order to obtain maximum absorbance and minimum background values, the operational parameters were optimized [7,8].

RESULTS

Calibration curves showed good linearity over the entire range of concentrations with acceptable coefficients ($r^2 >0.9$). Validation data (n ≥5) obtained for the selected metals in honey were shown in *Table 1*. The attained LODs are sufficiently low for honey safety monitoring purposes considering the maximum metal levels established in honey by the European Commission Regulation. The accuracy of the method was checked by spike recovery experiments. All measurements were performed, at least, in triplicate. The recovery values obtained by spiking the honey samples with Cd, Pb, Cu, Fe, Zn, Al and Hg standards, ranged between 92% and 101%. Analytical blanks and standards were analyzed daily and regularly along with samples to check instrument performance.

Table 1. *Validation data (n≥ 5) obtained for the select/ed metals in honey*
Tablo 1. *Ballarda, belirlenen metallerin validasyon verileri (n≥ 5)*

Metal	Linear Range (µg/L)	Correlation Coefficient (r²)	Limit of Detection (LOD) (µg/kg)	Limit of Quantification (LOQ) (µg/kg)	Recovery (%)	Relative Standard Deviation (RSD)%, n=3
Cd	0.25-1.25	0.9975	0.03	0.09	94	4
Pb	3.0-30.0	0.9878	1.3	3.67	99	3
Fe	0.2-06	0.9992	0.9	2.3	98	5
Zn	0.10-0.50	0.9583	0.05	0.17	101	8
Al	15-30	0.9694	7.0	22.1	97	9
Hg	1.0-5.0	0.9999	0.4	1.3	92	5
Cu	0.1-0.5	0.9957	1.2	3.36	98	6

Table 2. *Metal concentrations (mean and range; (mg/kg, wet weight) in honey*
Tablo 2. *Ballardaki metal konsantrasyonları sonuçları (ortalama, maks. ve min.,mg/kg, yaş ağırlık)*

Metal	Metal Concentration			SD (Standard Deviation)	Standard Error Mean (SEM)
	Mean	Minimum	Maximum		
Cd	0.343	0.216	1.553	0.205	0.021
Pb	1.101	0.699	12.300	1.277	0.128
Fe	41.13	13.45	97.30	22.87	2.29
Zn	6.76	3.82	17.96	3.88	0.39
Al	1.490	0.038	4.570	0.648	0.065
Hg	0.618	0.250	0.852	0.288	0.029
Cu	0.06	0.011	0.098	0.028	0.003

Elemental concentrations were determined on wet weight bases. Mean, minimum and maximum value of each heavy metal for the honey samples are reported in *Table 2*. As can be seen from these data most abundant elements in our honey samples are Fe and Zn with the mean values 41.13 mg kg and 6.79 mg kg, respectively. Since the average honey consumption in Turkey is 1.1 kg per year; consumed heavy metal contaminants were still found to be below the risk.

DISCUSSION

In Turkey there is no specific legislation on honey's metal contents. In Turkish Food Codex Regulation on Contaminants in Foodstuffs, only maximum limits for Pb, Cd and Hg exists for some foods including milk, meat, fish and seafoods, cereals, vegetables, fruit and fruit juices and food supplements. Maximum Pb, Cd and Hg levels are identified between 0.020 and 3 mg kg^{-1}, 0.050 and 3 mg kg^{-1} and 0.10 and 0.50 mg kg^{-1} respectively, for different foods. In the current study, the levels were found to be below the limits set for other foodstuff as mentioned [9]. The Joint FAO-World Health Organization Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) for Pb as 0.025 mg kg^{-1} body weight (bw), as 0.007 mg kg^{-1} bw for Cd and for Hg as 1.6 μg kg^{-1} body weight week. When the mean consumption of honey in a diet was taken in account, our results showed that the level of these metals are tolerable [10]. Generally our results were found to be compatible with those reported from Turkey. Yılmaz and Yavuz [11] detected the contents of Na, K, Ca, Mg, Cu, Fe, Mn, Zn and Co in 30 samples of honey collected from different parts of south-eastern Anatolia, Turkey by atomic absorption spectrometer. The mean values for Cu, Fe and Zn were 1.8, 6.6, and 2.7 mg kg^{-1}, respectively. Tuzen et al.[12] reported that it was noticable that the honeys from the Marmara region (West Anatolia) showed high levels of Cu, Mn, Zn, Ni, Se and Fe contamination. The reason might be that the industry has been well developed in this area and possibly apiaries are located at a distance not far from the polluted habitat. In contrast, honeys from East Anatolia showed lower contents of Cu, Mn, Zn, Fe and Pb than the other honeys, due to the fact that this region does not have industrially polluted apiaries. Bilandzic et al.[13] reported that the levels of Pb determined in multifloral honey in Croatia were generally higher than concentrations obtained from other geographical origins in Europe. It was found that Pb levels in multifloral honeys in 2010 and 2011 were higher (189 μg kg^{-1} and 360 μg kg^{-1}) than previously determined values in the same region of Croatia. These high concentrations of Pb in multifloral honey samples in the central region may be related to the fact that this region has become more urban and that the network of motorways is growing every year. Perna et al.[14] determined the Cd, Pb, Cr, and As levels in nine areas of southern Italy. Pb (0.289 mg kg^{-1}), Cd (0.013 mg kg^{-1}) and Cr (0.707 mg kg^{-1}) levels in honeys from studied areas were influenced by local environmental conditions and results were known to be within the acceptable limits and lower than our findings. Only in one area Pb level was detected highly (1.390 mg kg), this linked to the petroleum extraction-related and touristic activities, high movement of vehicles, especially in the spring-summer period. In Saghaei et al.[15] study, metal levels detected from the honey collected from four different areas of Orumieh City, in Iran. The results indicated that Zn had highest concentration followed by Cr, Fe, Mn, Pb, Ni, Co and As.

In this study, Cd, Pb, Fe, Zn, Al, Hg and Cu levels were determined in a total of 100 honey samples collected from 15 different companies. Results showed that the metal levels were known to be within the acceptable limits; however there is no specific legislation on honey's heavy metal contents. To define the acceptable levels or criteria related to chemicals, potential enhanced exposures like honey must be take into consideration. These results indicate that, honey production is made in accordance with the regulations and it's under control. In Turkey, honey production areas are generally far from the industrial areas and the flora and soil are suitable for high quality honey production so as seen in our results, honey is safe for metals which are harmful for human health.

REFERENCES

1. Belitz HD, Grosch W, Schieberle P: Food Chemistry. Springer, Berlin, 2009.

2. Bogdanov S, Jurendic T, Sieber R, Gallmann P: Honey for nutrition and health: A review. *J Am Coll Nutr,* 27, 677-689, 2008. DOI: 10.1080/07315724.2008.10719745

3. Przybylowski P, Wilczyn´ska A: Honey as an environmental marker. *Food Chem,* 74, 289-291, 2001. DOI: 10.1016/S0308-8146 (01)00153-4

4. Pohl P: Determination of metal content in honey by atomic absorption and emission spectrometries. *Tren Anal Chem,* 28, 117-128, 2009. DOI: 10.1016/j.trac.2008.09.015

5. Lambert O, Piroux M, Puyo S, Thorin C, Larhantec M, Delbacc F, Pouliquen H: Bees, honey and pollen as sentinels for lead environmental contamination. *Environ Pollut,* 170, 254-259, 2012. DOI: 10.1016/j. envpol.2012.07.012

6. Kurnaz E, Filazi A: Determination of metal levels in the muscle tissue and livers of chickens. *Fresen Environ Bull,* 20 (11): 2896-2901, 2011.

7. Meeravali NN, Madhavi K, Manjusha R, Kumar SJ: Sequential extraction of platinum, cisplatin and carboplatin from environmental samples and pre-concentration/separation using vesicular coacervative extraction and determination by continuum source ETAAS. *Talanta,* 118, 37-44, 2014. DOI: 10.1016/j.talanta.2013.09.045

8. Filazi A, Baskaya R, Kum C, Hismiogullari SE: Metal concentrations in tissues of the Black Sea fish Mugil auratus from Sinop-Icliman, Turkey. *Hum Exp Toxicol,* 22, 85-87, 2003. DOI: 10.1191/0960327103ht323oa

9. Anonymous: Turkish Food Codex Regulation on Contaminants in Foodstuffs. 29.12.2011-28157, 2011.

10. Morais S, Garcia C, Lourdes F, Pereira M: Heavy Metals and Human Health. **In,** Oosthuizen (Ed): Environmental Health-Emerging Issues and Practice. 227-246, Intech, Croatia, 2012.

11. Yılmaz H, Yavuz O: Content of some trace metals in honey from South-Eastern Anatolia. *Food Chem,* 65, 475-476, 1999. DOI: 10.1016/S0308-8146(98)00205-2

12. Tuzen M, Silici S, Mendil D, Soylak M: Trace element levels in honeys from different regions of Turkey. *Food Chem,* 103, 325-333, 2007. DOI: 10.1016/j.foodchem.2006.07.053

13. Bilandzic N, Sedak M, Ðokic M, Kolanovic BS, Varenina I, Bozic D, Simic B, Konc̆urat A, Brstilo M: Lead content in multifloral honey from central croatia over a three-year period. *Bull Environ Contam Toxicol,* 88:985-989, 2012. DOI: 10.1007/s00128-012-0585-z

14. Perna A, Intaglietta I, Simonetti A, Gambacorta E: Metals in honeys from different areas of Southern Italy. *Bull Environ Contam Toxicol,* 92, 253-258, 2014. DOI: 10.1007/s00128-013-1177-2

15. Saghaei S, Ekici H, Demirbas M, Yarsan E, Tumer I: Determination of the metal contents of honey samples from Orumieh in Iran. *Kafkas Univ Vet Fak Derg*, 18, 281-284, 2012. DOI: 10.9775/kvfd.2011.5426