Study of Gamma Radiation in Honey from the Zacatecas State

Sonia A. Saucedo-Anaya, Ma. Cristina Zapata-Vázquez, José L. Pinedo-Vega, J. Ignacio Dávila-Rangel, Carlos Ríos-Martínez, Fernando Mireles-García.
Unidad Académica de Estudios Nucleares, U. A. Z.
Ciprés #10; Frac. La Peñuela; Zacatecas, Zac. 98060
ssaucedo@uaz.edu.mx; socri_maza@hotmail.com; jlpinedo@uaz.edu.mx; idavila@uaz.edu.mx; crios@uaz.edu.mx; fmireles@uaz.edu.mx;

Abstract

Radioactivity of honey samples from 10 municipalities of the Zacatecas State in Mexico was investigated by gamma spectrometry. The honey corresponds to the *prosopis laevigata* flowering. The purpose of the study was to estimate the background levels of natural radioactivity and to discard a possible contamination with the artificial ^{137}Cs in honey. Any naturally occurring radionuclide could be determined except for ^{40}K, which was quantified in 8 of the 10 samples, with an average in specific activity of 9.75 ± 1.8 Bq/kg. No signal for the energy of the anthropogenic radionuclide ^{137}Cs was observed, corroborating that the radiation levels are in good agreement with those reported for another honeys in the world.

1. INTRODUCTION

Honey is a sweet natural substance produced by honey bees (*Apis mellifera*) from flower nectar or honeydew. This complex mixture is the result of components coming from plants, honeybees and biochemical reactions during honey maturation [1][2]. Its composition is mainly of fructose, glucose, water, some proteins and lipids. Depending on the botanical and geographical origin, honey can also contain some major (e.g. Na, K, Ca, Mg, P, S) and minor elements (e.g. Al, Cu, Pb, Zn, Mn, Cd, Tl, Fe, Se, etc.). Among these elements is K with the highest concentration [1]. Elevated concentrations of toxic elements or heavy metals are related to anthropogenic activities that contaminate the air, water and soil around the hives [1]. The pH values of honey ranges between 3.5-5.5 due to the presence of organic acids and inorganic ions. The concentration of minerals is directly related with the conductivity values [2]. These and other physicochemical parameters allow the characterization of different honey types [1].

Honey is a food that provides energy, valuable nutriments and antioxidants. It is used as sweetener or preservative in foodstuff worldwide. But also it is considered in medical treatments due to its antibacterial, anti-inflammatory and healing properties [3-5]. Special attention is given to the treatment of wounds and disorders of skin [6-8].

Honeybees and theirs products are considered as bioindicators in the analysis of contaminants in the environment [9]. The reason is found in the fact that each insect visits hundreds of flowers and is in contact with the air and water around the hive during harvest or food searching, taking every dispersed contaminant in the environment into the products of the hive, (i.e. honey, wax, pollen). The analysis of these materials can provide then important information about pollution [10]. In this respect, several contaminants (i.e. pesticides [11], heavy metals [9][12-14]) have been through these biomarkers monitored. Concerning to radioactivity in the environment, several reports have been done to register natural radioactivity levels [15-17], as well as, to monitor the dispersion or decline of radionuclides from anthropogenic activities or nuclear accidents (i.e. Chernobyl and Fukushima) [18-21].

Taking in account that Mexico is one of the main honey exporters of the world, with a great variety of honeys and that Zacatecas State contributes to approximately the 2.5 % of the national honey production, which is destined to the local and national consume, but principally to exportation; in this work a radioactive analysis, through gamma spectrometry, of *prosopis laevigata* honey from 10 municipalities of the Zacatecas State were carried on in order to *i*) estimate the background levels of natural radioactivity, *ii*) discard a possible contamination with the artificial ^{137}Cs in honey and surroundings and *iii*) give an additional quality control parameter to the honey in this region.

2. MATERIALS AND METHODS

2.1. Sampling

Samples were collected from a stock of individual barrels, which are well identified with the zone of harvest. The honey corresponds to the *prosopis laevigata* flowering; harvested during May to June 2011 in ten different municipalities, see Figure 1. From each municipality two samples (one liter per each) were collected.

2.2. Gamma Spectrometry

Gamma spectrometry allows us to detect simultaneously many gamma-ray emitters without previous treatment of the sample. However especially care must to be taken by assume secular equilibrium for the members of natural decay series. For many matrices these radioactive equilibria are broken and not all can be restore at laboratory [16]. Considering that, the two honey samples of each municipality were well homogenized and 500 mL poured into Marinelli containers. The containers were sealed in order to avoid the loss of gas radon and the density of each sample was calculated. The samples were stored for at least 40 days before counting, to ensure the establishment of the equilibrium between ^{226}Ra and its short-lived decay products.

The gamma-ray spectrometer system consists of a GMX-25190-P-PLUS high purity germanium (HPGe) coaxial radiation detector with an efficiency of 25 % and a resolution of 1.81 keV (^{60}Co gamma-ray energy of 1.33 MeV), coupled to a TRUMP-PCI-2k card as multichannel analyzer using 1024 channels and a EG&G ORTEC GammaVision-32 software.

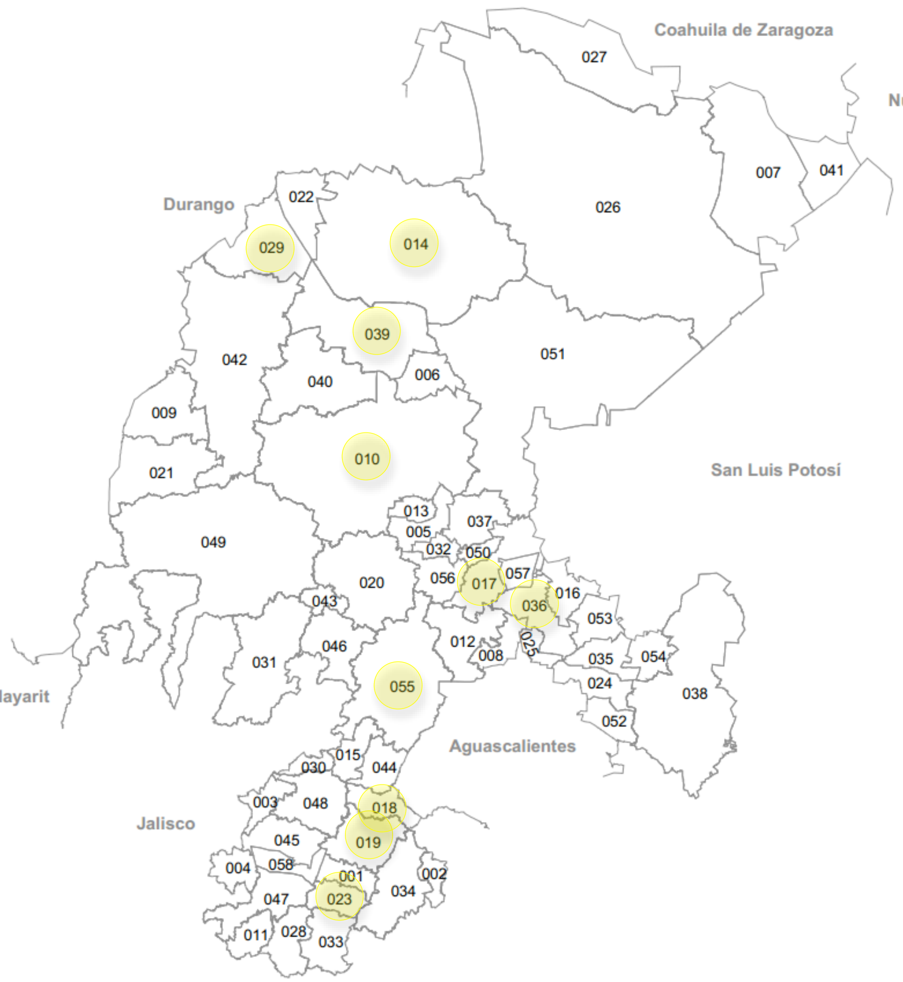

Figure 1. Honey harvest municipalities: 10) Fresnillo, 14) Gral. Francisco R. Murguía, 17) Guadalupe, 18) Huanusco, 19) Jalpa, 23) Juchipila, 29) Miguel Auza, 36) Ojocaliente, 39) Río Grande, 55) Villanueva.

2.2.1. Energy and efficiency calibration

A previously well-characterized soil sample was used as energy calibration source, using known gamma-ray energies of the natural occurring radionuclides present in the soil. Efficiency calibration was performed using a multinuclide standard source MULTLM479 certified in activity, with a nominal activity of 32.84 kBq ± 3.2%, in a 1000 mL water matrix and with a confidence level of 99%. For our experiment, an aliquot of 259 mL of the multinuclide standard was diluted to 500 mL and used as standard source. Counting efficiency is calculated using the equation (1).

$$\varepsilon_E = \frac{N_{Ei}}{A_{Ei} t Y} \tag{1}$$

Where ε_E is counting efficiency for each energy, N_{Ei} is the net area of the photopic, A_{Ei} is the activity of the radionuclide in the standard, t is counting time, and Y is the decay fraction of the measured radiation.

2.3.2. Counting

Standard source, background and samples were counting keeping the same geometry and counting parameters (counting time: 120000 s, negative voltage: -2000 v).

2.3.3. Detection limit (L_D), minimum detectable activity (MDA) and activity determination

An *a priori* evaluation of assay sensitivity of an instrument for a particular analysis is always need. The L_D is the lowest quantity of a substance that can be distinguished from an absence of substance and can be obtained by equation (2) [22].

$$L_D = 2.71 + 4.65\sqrt{b} \tag{2}$$

Where: b is the background radiation for each photopic. The MDA correspond to the minimum number of counts from the source needed to ensure a measurement with a confidence level of 95%, which is calculated with equation (3).

$$MDA = \frac{L_D}{\varepsilon_E t Y} \tag{3}$$

The activity for each radionuclide can be calculated by equation (4).

$$A_{Ei} = \frac{N_{Ei}}{\varepsilon_E t Y w_s} \tag{4}$$

Where: w_s is sample weight in (kg).

3. RESULTS AND DISCUSSION

3.1. Samples

The different honey samples have similar density values with an average of 1.45 g/ml (see, Table I), which allow make comparisons in the registered activity of each sample. Moreover, this density value will not increase significantly the attenuation of gamma rays, so no correction must be done in that respect.

Table I. Calculated densities of honey samples

Sample Location	Density (g/ml)
Fresnillo	1.50
Guadalupe	1.45
Huanusco	1.44
Jalpa	1.47
Juchipila	1.48
Miguel Auza	1.47
Gral. Francisco R. Murguía	1.45
Ojocaliente	1.38
Río Grande	1.40
Villanueva	1.43

3.2. Calibration of the gamma spectrometric system

For the energy calibration of the spectrometric system, thirteen known gamma-ray energies of the natural occurring radionuclides present in the calibration source were used (see Table II). Energy-channel correlation is $R^2 = 0.999$ and the linear fit is described by equation (5).

$$E = 1.632C - 4.288 \quad (5)$$

As mentioned before, a multinuclide standard source MULTLM479 certified in activity was used for calibration in efficiency. At the time of the counting, the only three detectable radionuclides in the standard source were ^{241}Am, ^{137}Cs and ^{60}Co. So for the calibration only the last three of the four measured energies were considered to build the calibration curve, which is fitted to the potential equation (6) with a $R^2 = 0.999$.

$$\varepsilon_i = 8.4228 E_i^{-0.97} \quad (6)$$

Table II. Energy calibration

Radionuclide	Channel	Energy (keV)
^{226}Ra	116.46	185.99
^{212}Pb	149.28	238.63
^{214}Pb	183.44	295.22
^{208}Tl	359.95	583.14
^{214}Bi	375.98	609.32
^{137}Cs	408.17	661.66
^{212}Bi	448.36	727.17
^{228}Ac	560.92	911.07
^{228}Ac	597.00	968.90
^{214}Bi	689.20	1120.28
^{214}Bi	761.46	1238.11
^{214}Bi	846.93	1377.63
^{40}K	898.04	1460.75

3.3. Radiation Measurements

In eight of the ten samples only for ^{40}K the MDA was smaller than the measured activity. In Table III are reported the values of the MDA (in Bq/kg of sample) and specific activity for the radionuclide ^{40}K. The counting efficiency for the energy of the ^{40}K nuclide was 0.0072. The samples from the Jalpa and Ojocaliente sites could not be quantified. All other samples have in average a specific activity of 9.75 ± 1.8 Bq/kg from ^{40}K, which is bellow of the mean activity value reported in other studies, see Table IV.

Table III. MDA and Specific activity for ^{40}K

Sample Location	MDA (Bq/kg)	Specific activity (Bq/kg)
Fresnillo	6.57 ±0.03	6.99 ± 2.15
Guadalupe	7.14 ± 0.04	9.98 ± 2.33
Huanusco	7.19 ± 0.04	13.75 ± 2.36
Jalpa	7.04 ±0.04	5.33 ± 2.29
Juchipila	6.99 ± 0.04	9.02 ± 2.28
Miguel Auza	7.06 ± 0.04	9.68 ± 2.31
Gral. Francisco R. Murguía	7.14 ± 0.04	11.94 ± 2.34
Ojocaliente	7.49 ± 0.04	6.79 ± 2.44
Río Grande	7.43 ± 0.04	8.29 ± 2.43
Villanueva	7.24 ± 0.04	8.33 ± 2.36

The correspond mean concentration of potassium is 213.01 mg/kg. This value is in the range of potassium reported (39.66 - 1349.34 mg/kg) for several honeys all over the word [1].

Table IV. Comparison of mean activities values and ranges of ^{40}K

Sample Location	Mean Specific Activity (Bq/kg)	Range (Bq/kg)
Yugoslavia [21]	14 ± 2	6.6 to 38
Poland [23]	36.06 ± 21.3	5.51 to 98.89
Italy [16]	28.1 ± 23.0	7.28 to 101
This study	9.75 ± 1.8	6.99 to 13.75

4. CONCLUSIONS

Monitoring of natural radionuclides in honey was performance by gamma-ray spectrometry. Typical radionuclides present in soil samples could be observed in all samples spectra, however the signal were below the calculated L_D, except for the signal of the ubiquitous ^{40}K, which signal was above even the MDA. In most of the samples ^{40}K could be quantified, given an average of specific activity of 9.75 ± 1.8 Bq/kg. No signal for the energy of the anthropogenic radionuclide ^{137}Cs was observed. Finally, these results estimate the background levels of natural radioactivity and discard a possible contamination with artificial radionuclides in honey, corroborating that the radiation levels are in good agreement with those reported for another honeys in the world.

REFERENCES

1. Solayman, Md.; Islam, Md. Asiful; Paul, Sudip; Ali, Yousuf; Khalil, Md. Ibrahim; Alam, Nadia & Hua Gan, Siew 2016 Physicochemical Properties, Minerals, Trace Elements, and Heavy Metals in Honey of Different Origins: A Comprehensive Review. *Comprehensive Reviews in Food Science and Food Safety*, **15**, p. 219-233.
2. Pita-Calvo, Consuelo & Vázquez, Manuel 2017 Differences between honeydew and blossom honeys: A review. *Trends in Food Science & Technology*, **59**, p. 79-87.
3. Al-Waili, Noori S.; Salom, Khelod; Butler, Glenn & Al Ghamdi, Ahmad A. 2011 Honey and Microbial Infections: A Review Supporting the Use of Honey for Microbial Control. *Journal of Medicinal Food*, **14**, p. 1079-1096.
4. Francis, Anna; Cho, Yeoungjee & Johnson, David W. 2015 Honey in the Prevention and Treatment of Infection in the CKD Population: A Narrative Review. *Evidence-Based Complementary and Alternative Medicine*, p. 1-8.
5. Devasvaran, Kogilavanee & Young, Yoke-Keong 2016 Anti-inflammatory and wound healing properties of Malaysia Tualang honey. *Current Science*, **110**, p. 47-51.

6. Vandamme, L.; Heyneman, A.; Hoeksema, H.; Verbelen, J. & Monstrey, S. 2013 Honey in modern wound care: A systematic review. *Burns*, **39**, p. 1514-1525.
7. Alam, Fahmida; Islam, Md. Asiful, Huan Gan, Siew & Khalil, Md. Ibrahim. 2015 Honey: A Potencial Therapeutic Agent for Managing Diabetic Wounds. *Evidence-Based Complementary and Alternative Medicine*, p. 1-16.
8. McLoone, Pauline; Warnock, Mary & Fyfe Lorna 2016 Honey: A realistic antimicrobial for disorders of skin. *Journal of Microbiology, Immunology and Infection*, **49**, p. 161-167.
9. Conti, Marcelo Enrique & Botrè, Francesco 2001 Honeybees and their products as potential bioindicators of heavy metals contamination. *Environmental Monitoring and Assessment,* **69**, p. 267-282.
10. Panatto, Donatella; Gasparini, Roberto; Lai, Piero; Rovatti, Paola & Gallelli Giovanni 2007 Long-term decline of ^{137}Cs concentration in honey in the second decade after Chernobyl accident. *Science of the Total Environment*, **382**, p. 147-152.
11. Souza-Tette, Patrícia Amaral; Rocha-Guidi, Letícia; de Abreu-Glória, Maria Beatriz & Fernandes, Christian 2016 Pesticides in honey: A review on chromatographic analytical methods. *Talanta*, **149**, p. 124-141.
12. Buildini, Pier Luigi; Cavalli, Silvano; Mevoli, Anna & Sharma, Jawahar Lal 2001 Ion chromatographic and voltammetric determination of heavy and transition metals in honey. *Food Chemistry*, **73**, p. 487-495.
13. Tuzen, M.; Silici, S.; Mendil, D. & Soylak, M. 2007 Trace element levels in honey from different regions of Turkey. *Food Chemistry*, **103**, p. 325-330.
14. Pisani, Anastasia; Protano, Giuseppe & Riccobono, Francesco 2008 Minor and trace elements in different honey types produced in Siena County (Italy). *Food Chemistry*, **107**, p. 1553-1560.
15. Al-Masri, M. S.; Mukallati, H.; Al-Hamwi, A.; Khalili, H.; Hassan, M.; Assaf, H.; Amin, Y. & Nashawati, A. 2004 Natural radionuclides in Syrian diet and their daily intake. *Journal of Radioanalytical and Nuclear Chemistry*, **260**, p. 405-412.
16. Meli, Assunta Maria; Desideri, Donatella, Roselli, Carla; Feduzi, Laura & Benedetti, Claudio 2016 Radioactivity in honey of the central Italy. *Food Chemistry*, **202**, p. 349-355.
17. Brandhoff, P. N.; van Bourgondiën, M. J.; Onstenk, C. G. M.; van Avezathe, A. Vos & Peters R. J. B. 2016 Operation and performance of a National Monitoring Network for Radioactivity in Food. *Food Control*, **64**, p. 87-97.
18. Tonelli, D.; Gattavecchia, E.; Ghini, S.; Porrini, C. & Celli, G. 1990 Honey bees and their products as indicators of environmental radioactive pollution. *Journal of Radioanalytical and Nuclear Chemistry*, **141**, p. 427-436.
19. Constantinescu, B; Galeriu, D.; Ivanov, E.; Pascovici, G. & Plostinaru, D. 1990 ^{131}I, ^{134}Cs and ^{137}Cs concentrations in 1986 for some roumanian foodstuffs. *Journal of Radioanalytical and Nuclear Chemistry, Letters*, **144**, p. 429-437.
20. Assmann-Werthmüller, U.; Werthmüller, K. & Molzahn, D. 1991 Cesium contamination of heather honey. *Journal of Radioanalytical and Nuclear Chemistry*, **149**, p. 123-129.
21. Cokesa, Dj. M.; Markovic, M. M.; Solesa, M. I.; Adzic, P. R.; Skoro, G. P.; Milonjic, S. K. & Kukoc, A. H. 1995 Determination of ^{40}K and ^{137}Cs concentration in selected honey samples. *Journal of Radioanalytical and Nuclear Chemistry, Letters*, **199**, p. 465-469.
22. Currie, Lloyd A. 1968 Limits of Qualitative Detection and Quantitative Determination, Aplication to Radiochemistry. *Analytical Chemistry*, **40**, p. 586-593.

23. Borawska, Maria H.; Kapala, Jacek; Puscion-Jakubik, Anna; Horembala, Justyna; Markiewicz-Zukowska, Renata 2013 Radioactivity of honeys from Poland after the Fukushima accident. *Bulletin of Environmental Contamination and Toxicology*, **91**, p. 489-492.