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Measurement of ^{238}U, ^{232}Th, ^{87}Rb, and ^{40}K in Honey by ICP-Mass Spectrometry

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Abstract. The elemental concentrations of U, Th, Rb and K were measured in some honey samples of different origins by ICP-mass spectrometry. The samples were collected from local markets and producers in Riyadh city. The activity concentrations of the main radioisotopes of known natural abundance, ^{238}U, ^{232}Th, ^{87}Rb, and ^{40}K were calculated using mass-activity relationship. For quality control, the technique was tested against standard reference materials. The results showed that the activity levels are mainly related to ^{40}K.

Introduction

Honey is widely consumed as is or as a sugar substitute. Along with its acceptance as a delightful food and for cultural reasons[1], Saudi Arabia and the region are major consumers of honey. Most of honey consumed in Saudi Arabia is imported from various countries around the world. Local production is rapidly expanding especially in agricultural regions, south of the country.

Honey has been proposed as an indicator for environmental contamination[2]. Elemental concentration of honey varies substantially depending on plant, bee species, environmental factors and production practices[3,4]. Because of variable concentrations of natural radioactive elements in the environment, honeys of different origins are expected to contain variable radioactivity levels. Beyond natural radioactivity, honey along with pollen and bee tissues can be used to monitor radioactive contamination resulting from fallout of radioactive elements or from their environmental releases. Examples can be found in studies conducted after the Chernobyl accident and at areas near nuclear reactors[5, 6].

Gamma-ray spectroscopy, alpha spectrometry and liquid scintillation counting can be adequately used to monitor low-level radioactivity. However, low-level radioactivity monitoring requires special settings, special skills, and can be very expensive. With established analytical labs one can use atomic absorption and atomic emission techniques to determine elemental mass concentrations. Mass concentration can be used to calculate the activity concentration of some naturally-occurring radioisotopes of known natural abundance.

ICP-MS is a powerful (non-nuclear) technique for elemental determination and can be used to determine most elements of the periodic table with a detection limit in the range of few parts per billion (ppb). This technique was used in this study to determine concentrations of some radioisotopes in some honey samples of different origins, collected from the Saudi market in Riyadh city.

Experimental

Sampling

Honey samples were collected from the Saudi market as well as from some local producers. Imported samples were selected from brands of high sales in the market. Locally produced samples were selected from the Riyadh area only. Sample origin and related information are presented in Table 1.

TABLE 1. Brand name and origin of analyzed samples.

Sample	Brand name	Origin	Packed in	Date
1	World's	Australia	Singapore	1999
2	Starry	Australia	Singapore	2000
3	Bonne Maman	France	France	2000
4	Amarosa	Australia	Australian	1998
5	Langnese	Germany	Germany	1999
6	Al Reef	Australia	Switzerland	2000
7	Non	Egypt	Egypt	1999
8	Non	Kazakhstan	Kazakhstan	2000
9	Sary	?	Saudi Arabia	2000
10	Al-Shifa	?	Saudi Arabia	2000
11	Capilano	Australia	Australian	1999
12	Nectaflor (Blossom)	Switzerland	Switzerland	2000
13	Dutch Gold	USA	USA	1999
14	Nectaflor (Forest)	Switzerland	Switzerland	2000
15	Nadic	Saudi Arabia	Saudi Arabia	2000
16	Kacst	Saudi Arabia	Saudi Arabia	2000

Sample Digestion

About 0.1 g of honey was weighed into PTFE bombs; a 6 ml of 65% nitric acid was added along with 1 ml of 30% hydrogen peroxide. The samples were digested in a Milestone microwave, ETHOS1600, system. After digestion samples were made up to 30 ml with deionized water. Relatively high recoveries for all elements were reported in PTFE bombs using either a pressure cooker or a microwave oven[7].

Analysis

Analysis was performed by a Perkin-Elmer Sciex Instruments multi-element ICP-mass spectrometer, type ELAN6100. The ELAN provides a fully automated method that allows determination of 81 elements in an unknown in a single measurement. This method was used to perform a rapid survey determination to identify elemental composition of honey samples. Based on this preliminary determination a fully quantitative analysis using appropriate standards was performed[8]. From the elemental mass concentration, the activity concentration of the radionuclide of interest can be calculated using the following mass-activity relationship:

$$A = \frac{w \times a \times 6.022 \times 10^{23} \times 0.693}{M \times t_{1/2}}$$

Where, A is the activity concentration (Bq/kg)

w = the elemental mass concentration (g/kg)

$t_{1/2}$ = the half-life of the radionuclide (seconds)

a = the natural abundance of the radionuclide (%)

M = the atomic mass of the element

Standards and Reference Material

For full quantitative analysis the system was calibrated using multi-element standards for all elements of interest. Internal standard was prepared from stock solution of Rh. All standards were supplied by Perkin-Elmer.

To assess the analytical process, Standard Reference Material (SRM) rice flour SRM 1568a from the National Institute of Standards and Technology (NIST), and milk powder SRM IAEA-153 provided by International Atomic Energy Agency, were used. Analytical results along with certified values of trace elements for these standards are presented in Tables 2 and 3.

TABLE 2. Analysis data for the standard reference material SRM 1568a.

Element	Certified values		Measured values	
	Concentration (ppm)	Error	Concentration (ppm)	%RSD§
Mn	20.0	1.6	20.06	0.2
Cu	2.4	0.3	3.42	1.7
Zn	19.4	0.5	12.60	1.4
As	0.29	0.03	0.24	4.6
Se	0.38	0.04	0.07	88
Rb	6.14	0.09	6.43	0.4
Cd	0.022	0.002	0.023	9.7
Hg	0.0058	0.0005	0.013	6.4

§Relative standard deviation

TABLE 3. Analysis data for the standard reference material SRM IAEA-153.

Element	Certified values		Measured values	
	Concentration (ppm) (ppm)	95% confidence interval	Concentration (ppm)	%RSD§
Na	4180	3870-4440	4262.94	0.7
Mg	1060	1000-1150	1026.56	1
K	17620	16480-18760	18094.97	0.8
Ca	12870	12540-13170	9118.67	0.6
Mn	0.19*	0.12-0.26	0.32	1.2
Cu	0.57*	0.38-0.78	0.92	0.8
Zn	39.56	37.66-41.23	28.72	1.4
Rb	17.82	12.27-16.10	17.82	0.9
Sr	4.69*	3.49-4.73	4.69	0.6

*Information values
§Relative standard deviation

Naturally Occurring Radioactive Materials

Naturally occurring radioactive materials often referred to as NORM consist of isotopes of cosmogenic and terrestrial origins. From a biological viewpoint ^{3}H and ^{14}C are important among the isotopes of cosmogenic origin. Important singly occurring terrestrial isotopes include ^{40}K, ^{87}Rb. In addition ^{238}U, ^{226}Ra and ^{232}Th are important members of the natural decay series[9]. Decay properties of these radioisotopes are presented in Table 4.

TABLE 4. Decay properties of some naturally occurring radioisotopes.

Isotope	$t_{1/2}$ (years)	Decay mode	Isotopic abundance
^{3}H	12.26	β^-	
^{14}C	5760	β^-	
^{40}K	1.3×10^{9}	β^-, EC	0.118%
^{87}Rb	4.7×10^{10}	β^-	27.83%
^{238}U	4.5×10^{9}	α	99.27%
^{232}Th	1.4×10^{10}	α	100%

Results and Discussion

The elemental concentration of K, Rb, Th, and U determined in this study are presented in Table 5. Based on the elemental concentrations and the isotopic abundance, the activity concentration of ^{40}K, ^{87}Rb, ^{238}U and ^{232}Th are calculated and presented in Table 6. ^{226}Ra has no constant abundance; hence its activity concentration can not be calculated from total radium concentration.

TABLE 5. Elemental concentrations (ppb).

	Sample \ Element	K	Rb	Th	U
Imported honey	1	1003043(1)	1606(1)	<0.4	8(2)
	2	635960(1)	1469(1)	–	14(2)
	3	153663(2)	158(1)	<1	26(2)
	4	835261(1)	861(1)	<2	20(4)
	5	765246(1)	1182(0.1)	<0.8	19(3)
	6	394517(1)	716(1)	<1.3	43(3)
	7	2748463(1)	406(1)	<1.3	4(2)
	8	73248(1)	180(0.3)	<1.9	16(5)
	11	908202(0.2)	1333(1)	<1.1	21(2)
	12	665798(1)	1022(1)	–	29(3)
	13	291473(1)	328(1)	<0.4	66(1)
	14	2861157(0.2)	4430(0.2)	–	34(2)
Local honey	9	359923(0.4)	557(1)	<0.4	57(3)
	10	263965(0.8)	275(1)	<0.4	17(2)
	15	584382(0.9)	375(0.1)	–	151(1)
	16	1792099(0.8)	647(1)	<2	101(2)

Values in parentheses are % relative standard deviation

From Table 6 it is obvious that ^{40}K is responsible for most of the activity of honey. There are wide differences in total honey activity for different samples which is expected. This is due to widespread difference of potassium concentration in the analyzed honey samples. The differences in potassium concentration can be attributed to environmental, botanical, and bee species factors.

TABLE 6. Activity (Bq/kg).

	Element / Sample	^{40}K	^{87}Rb	^{238}U	^{232}Th
Imported honey	1	301.27	1.447	0.098	<0.002
	2	191.02	1.323	0.172	–
	3	46.15	0.142	0.319	<0.004
	4	250.88	0.776	0.245	<0.008
	5	229.85	1.065	0.233	<0.003
	6	118.5	0.645	0.528	<0.005
	7	825.5	0.366	0.049	<0.005
	8	22.0	0.162	0.196	<0.008
	11	272.79	1.201	0.258	<0.004
	12	199.98	0.921	0.356	–
	13	87.55	0.295	0.810	<0.002
	14	859.37	3.991	0.417	–
Local honey	9	108.11	0.502	0.699	<0.002
	10	79.28	0.248	0.209	<0.002
	15	175.52	0.338	1.853	–
	16	538.27	0.583	1.239	<0.008

Except for sample 14 which shows an activity of about four, ^{87}Rb activity is less than 1 Bq/kg in most cases. Sample 14 also shows the highest activity of ^{40}K. Potassium and rubidium belong to the same group in the periodic table; higher concentrations of both elements in the soil and the environment around the production area may be the reason for higher concentrations in the honey produced in the region.

The activity concentration of ^{238}U was less than 1 Bq/kg of honey of all samples except for samples 15 and 16 which show higher concentrations. ^{238}U activity concentration in samples 15 and 16 is 1.85 and 1.24 Bq/kg, respectively. This may be due to environmental factors.

To single out a specific reason for an increased activity of certain isotope extensive studies of soil, air, plant, and bee species are required. It is worth mentioning that concentrations of Cs for all samples were in the range of few ppb[10], since natural caesium is 100% non radioactive no radioactivity contribution is attributed to Cs. To monitor contamination of non-natural radioisotopes one should resort to nuclear means.

Conclusion

^{238}U, ^{232}Th, ^{87}Rb, and ^{40}K are measured in some honey samples of different origins by ICP-mass spectrometry. The obtained results showed that the activity concentrations were in the normal levels in all samples. The activity levels for the measured radionuclides generally follow the sequence $^{40}K >> {}^{87}Rb >\approx {}^{238}U >= {}^{232}Th$. The activity levels are mainly related to ^{40}K because honey is rich in natural potassium.

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قياس ^{87}Rb, ^{232}Th, ^{238}U, ^{40}K في العسل بتقنية ICP-MS

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المستخلص. تم قياس تراكيز عناصر U, Th, Rb, K في بعض عينات العسل مختلفة المنشأ بواسطة تقنية ICP-MS. جمعت العينات من الأسواق المحلية ومن بعض المنتجين في مدينة الرياض. طبقت العلاقة بين الكتلة والنشاط الإشعاعي لحساب النشاط الإشعاعي للنظائر الأساسية ^{238}U, ^{232}Th, ^{87}Rb, ^{40}K تمت معايرة نظام القياس باستخدام مواد مرجعية. توضح النتائج أن مستوى النشاط الإشعاعي مرتبط أساسا مع ^{40}K.