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Evaluation of Lead, Cadmium and Copper Concentrations in Bee Honey and Edible Molasses

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Abstract: Problem statement: Content of Cadmium, lead and copper in 26 bee honey samples from different places of Assiut governorate (south of Egypt) and three different botanical origins (Clover, Multi-flower and Citrus) in addition to four edible molasses samples from Egypt market were evaluated by Differential Pulse Anodic Stripping Voltammetry (DPASV) in Briton-Robinson buffer solution at pH ~ 2.1, as well as atomic absorption spectrometry after wet digestion. **Approach:** The optimal deposition potentials and times for the detection of these metal ions in all sample solutions have been studied. **Results:** The concentration of each metal ion was determined by the standard addition method. The statistical parameters i.e., slope, standard deviation, correlation coefficient and confidence have been calculated. **Conclusion/Recommendations:** The results obtained using stripping voltammetry indicate that the average concentration of Cu ions ranged from 0.085-0.987 μg g^{-1}. In addition, the average concentrations of Cd and Pb ions ranged 0.001-0.077 and 0.006-1.640 μg g^{-1}; respectively. On the other hand, the average concentrations obtained using atomic absorption spectrometry of the same element mentioned above ranged from 0.077-0.991 μg g^{-1} for Cu; 0.001-0.087 μg g^{-1} for Cd and 0.007-1.650 μg g^{-1} for Pb.

Key words: Stripping voltammetry, honey, molasses, biological indicator

INTRODUCTION

Honey is a quick, safe and natural energy giver because its simple sugar is quickly absorbed into the blood stream, honey is an easily digestible foodstuff containing a range of nutritiously important complementary elements. Besides a high content of a range of saccharides, there are also organic acids, amino acids, mineral matters, colors, aromatic substances and a trace amount of fats (Bogdanov *et al*., 1999). Besides these, honey contains very valuable but unstable compounds, such as enzymes, substance of hormonal character, some vitamins and a few minor compounds (Yilmaz and Yavuz, 1999). Honey contaminations by heavy metals (especially Pd, Cd and Cu) that are widely spread in our environment are the result of:

- The location of colonies in industrial zones or other areas with considerable air pollution such as cities, can lead to considerable contamination of various hive products with noxious or toxic chemical. Agricultural use of toxic chemicals is another common and very likely source of contamination; further contamination may results from dirty water source and non-floral sugar source (Antonescu and Mateescu, 2001)
- The use of unpleasant smelling chemicals to drive bees away is a technique preferred by many beekeepers because it is quick and easy (Dadant and Sons, 1992)
- Containers previously used for toxic chemicals, oil or petroleum products or vessels doesn't manufacture for food preservation should never be used for storing honey, because it is become a source of honey contamination by heavy metals

Several authors have indicated that bee and their products may be used as biological indicator (Fernandez *et al*., 1994; Sanna *et al*., 2000; Buldini *et al*., 2001; Bogdanov *et al*., 2003; Fredes and Montenegro, 2006).

Copper is both vital and toxic for many biological system, it is critical for energy production in the cells, also involved in nerve conduction, connective tissue, the cardiovascular system and the immune system. Copper is closely related to estrogen metabolism and is required for women's fertility and to maintain pregnancy. Copper stimulates production of the neurotransmitters epinephrine, norepinephrine and dopamine. It is also required for monoamine oxidase, an enzyme related to serotonin production. Also excess

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copper may be absorbed in the intestinal tissues which lead to intestinal disorders, impaired healing and reduced resistance to infections (Wilson, 1998).

Cadmium is one of the few elements that have no constructive purpose in the human body. This elements and solution of its compound are extremely toxic even in low concentration and will bioaccumulation in organisms and ecosystems. One possible reason for its toxicity is that it interferes with the action of zinc-containing enzymes. Cadmium may also interfere with biological processes containing magnesium and calcium (Lide, 2005; Clarkson, 1988). Its toxicity threatens the health of the body by weakened immune system, Kidney disease and live damage, Effects may include emphysema, cancer and a shortened life span (Lide, 2005).

Lead has no know biological role in the body. Its toxicity comes from its ability to mimic other biologically important metals, the most notable of which are calcium, iron and zinc. Lead is able to bind to and interact with the same proteins and molecules as these metals, but after displacement, those molecules function differently and fail to carry out the same reactions, such as in producing enzymes necessary for certain biological processes. Most lead poisoning symptoms are thought to occur by interfering with an essential enzyme Delta-aminolevulinic acid dehydratase, or ALAD (is a zinc-binding protein which is important in the biosynthesis of heme, the cofactor found in hemoglobin) (Simon and Hudes, 1999). It inhibits several enzymes critical to the synthesis of heme, causing a decrease in blood hemoglobin and interferes with a hormonal form of vitamin D, which affects multiple processes in the body, including cell maturation and skeletal growth. Lead can also cause hypertension, reproductive toxicity and developmental effects. Lead exposure can lead to renal effects such as fanconi-like syndromes, chronic nephropathy and gout (Batuman *et al*., 1981).

Recently, several methods of analysis were done for determination of cadmium, lead and copper, e.g., by stripping voltammetry (Sanna *et al*., 2000; Buldini *et al*., 2001; Li *et al*., 1995), potentiometric stripping analysis (Munoz and Palmero, 2006), atomic absorption spectroscopy (Bogdanov *et al*., 1999; Antonescu and Mateescu, 2001; Vinas *et al*., 1997; Rodriguez-García *et al*., 2003; Taddia *et al*., 2004; Tuzen and Soylak, 2005; Ajtony *et al*., 2007), inductively coupled plasma atomic emission spectrometry (Carol i *et al*., 1999; Ioannidou *et al*., 2005; Terrab *et al*., 2005). Inductively coupled plasma mass spectrometry (Packer and Gine, 2001), inductively coupled plasma optical emission spectrometry (Fredes and Montenegro, 2006; Lachman *et al*., 2007), total reflection X-ray fluorescence spectrometry (Kump *et al*., 1996).

MATERIALS AND METHODS

Apparatus: All glassware was soaked in 10% (v/v) HNO_3 for 24 h and rinsed three times with distilled water and then in redistilled water before use:

- Polarographic analyzer/stripping voltammeter. Anodic differential pulse stripping voltammograms were recorded with an EG and G. Princeton Applied Research Crop. (PAR; Princeton, NJ) model 264 A stripping analyzer, coupled with a PAR 303 A Hanging Mercury Drop Electrode (HMDE). The polarographic cell (PAR Model K0060) was fitted with Ag/AgCl saturated KCl and used as a reference electrode with a platinum wire as a counter (auxiliary) electrode. A PAR 305 magnetic stirrer was connected to the 303A SMDE. A PAR Model RE 0151X-Y recorder was used to collect experimental data. Before measurements the sample solution was deaereated by bubbling for 16 minutes with nitrogen. During measurements, an inert atmosphere over the solution was maintained by flushing with nitrogen. During the deposition step, the solution was stirred automatically, followed by a quiescent period of 15 sec before scanning
- PH was measured with a Fischer Scientific (Pittsburgh, PA, USA) Digital pH Meter Model 810
- GBC 906 atomic absorption spectrophotometer was used for Cu(II) measurement at Wavelength 324.7 nm, band-pass 0.7 nm and lamp current 6.0 mA and a AA-6800 Shimadzu (GFA-EX7) Graphite Furnace atomic absorption spectrophotometer was used for Cd(II) and Pb(II) determination at band-pass 0.7 nm, lamp current 8.0 mA and Wavelength 228.9 and 283.2 nm respectively

Solution and reagents: All reagents are of analytical grade. The following solutions were prepared with bidistilled water:

- Solution of each Cd(II), Pb(II) and Cu(II) were prepared respectively by dissolving the required amounts of $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)$ and $Cu(NO_3)_2.2H_2O$ in bidistilled water. The resulting solutions were then standardized (Vogel and Basset, 1978). Solutions of lower concentrations were prepared by accurate dilution

Table 1: The sources and cadmium content of different clover (BC_x), multi-flower (MC_x) and citrus (OC_x) honey samples and edible molasses samples (EM_x) (a mean value ± standard deviation for n = 5 at the 95% confidence level)

Samples number	Geog. sources	T_d (sec)	Cadmium content (mean ± SD) μg g^{-1}	Regression parameter: Correction coefficient	Regression parameter: Confidence Higher	Regression parameter: Confidence Lower	Cadmium content (mean ± SD) μg g^{-1} (GFAAS)
BC_1	Assiut	120	0.027±0.00600	0.9998	0.0350	0.0190	0.030±0.006
BC_2	Sedfa	45	0.055±0.00300	0.9996	0.0590	0.0510	0.051±0.001
BC_3	Abutig	90	0.042±0.00500	0.9993	0.0480	0.0360	0.044±0.007
BC_4	Dairut	90	0.052±0.00300	0.9995	0.0560	0.0520	0.055±0.004
BC_5	Al-Qusiya	120	0.029±0.00200	0.9999	0.0320	0.0270	0.030±0.001
BC_6	Manfalut	120	0.042±0.00600	0.9998	0.0490	0.0350	0.044±0.002
BC_7	Al-Ghanayem	60	0.013±0.00100	0.9998	0.0140	0.0120	0.014±0.001
BC_8	Abnub	120	0.024±0.00100	0.9999	0.0250	0.0230	0.028±0.005
BC_9	Sahil Salem	120	0.022±0.00200	0.9996	0.0250	0.0190	0.021±0.002
BC_{10}	Al-Badary	90	0.047±0.00200	0.9995	0.0490	0.0450	0.052±0.005
BC_{11}	Al-Fateh	30	0.042±0.00300	0.9995	0.0460	0.0380	0.043±0.008
BC_{12}	Mangapad	120	0.012±0.00100	0.9992	0.0130	0.0110	0.013±0.003
MC_1	Assiut	120	0.013±0.00100	0.9992	0.0140	0.0120	0.012±0.001
MC_2	Sedfa	120	0.023±0.00100	1.0000	0.0240	0.0220	0.026±0.006
MC_3	Abutig	45	0.033±0.00100	0.9999	0.0340	0.0320	0.030±0.009
MC_4	Dairut	120	0.051±0.00200	0.9993	0.0530	0.0480	0.051±0.002
MC_5	Al-Qusiya	120	0.043±0.00200	0.9992	0.0460	0.0410	0.047±0.008
MC_6	Manfalut	30	0.077±0.00400	0.9997	0.0820	0.0720	0.087±0.005
MC_7	Al-Ghanayem	120	0.0044±0.0001	1.0000	0.0045	0.0043	0.005±0.001
MC_8	Abnub	60	0.0067±0.0003	0.9992	0.0070	0.0063	0.007±0.001
MC_9	Sahil Salem	120	0.014±0.00100	0.9993	0.0150	0.0130	0.013±0.005
MC_{10}	Al-Badary	60	0.016±0.00200	0.9997	0.0190	0.0140	0.015±0.002
MC_{11}	Al-Fateh	60	0.008±0.00100	0.9996	0.0090	0.0070	0.008±0.001
MC_{12}	Mangapad	120	0.067±0.00300	0.9991	0.0710	0.0630	0.070±0.003
OC_1	Sahil Salem	120	0.048±0.00300	0.9997	0.0520	0.0440	0.050±0.001
OC_2	Al-Badary	30	0.055±0.00600	0.9998	0.0630	0.0480	0.052±0.007
EM_1	Al-Hana Al-Karma, Minia Dahab	60	0.066±0.00700	0.9995	0.0750	0.0570	0.068±0.002
EM_2	El-Seid, Mallawi, Minia	120	0.001±0.000100	0.9992	0.0011	0.0009	0.001±0.0001
EM_3	El-Kother Al-Khlood, Qena	90	0.061±0.00200	0.9994	0.0640	0.0590	0.061±0.0060
EM_4	Al-Temsah Al-Temsah, Tanta	120	0.010±0.00100	0.9995	0.0110	0.0090	0.010±0.0030

- Briton-Robinson buffer solution was prepared by dissolving 201 μL glacial acetic acid (AnalaR), 240 μL phosphoric acid (Merck) and 433 mg boric acid (BDH) in 500 ml measuring flask with bidistilled water (Ensafi *et al*., 2004).

Honey samples: Twenty-six bee honey samples were collected from Assiut governorate (south of Egypt) and four edible molasses as shown in Table 1.

Samples were collected in glass bottles and stored in dark prior to analysis.

Sample preparation: One gram of sample was treated with 10 mL of concentrated nitric acid, in a beaker, heating until nearly dry. This procedure was repeated with 15 mL of a 2:1 (HNO_3/$HClO_4$) mixture until complete mineralization. The residue was dissolved, at room temperature, in 1ml of 1M nitric acid, transferred to a 100 mL volumetric flask and diluted with bidistilled water (Fernandez-Torres *et al*., 2005). A control reagent blank was prepared in the same manner to determine the ultra trace impurities using the standard addition method as already used for the sample.

Analytical procedure: the following parameters were used to perform Differential Pulse Anodic Stripping Voltammetry (DPASV). Scan rate 10 mVs^{-1} with duration for 1 sec and pulse amplitude (ΔE) 25 mV.

For determination of Cd(II), Pb(II) and Cu(II) in bee honey and edible molasses samples in the same cell. 5 mL of each sample solution and 1 mL of 0.028 M Briton-Robinson buffer solution as supporting electrolyte were transferred into the electrolysis cell and completed to 10 mL using bidistilled water (pH ~ 2.1).

The solution was deaereated by passing pure nitrogen for 16 min. The deposition potential were controlled at (-0.75, -0.55 and -0.25 V Vs Ag/AgCl saturated KCl respectively) and applied to a fresh mercury drop while the solution was stirred. After the deposition step and further 15 sec. (equilibrium time) the voltammogram was recorded.

Different concentration from the standard metal ion (individually) were added to the cell using an automatic pipette (Volac 10-100 µL), while keeping the deposition time constant. The solution was stirred and purged with nitrogen for 30 sec. after each spike. The concentration of each Cd(II), Pb(II) and Cu(II) in the electrolytic cell was calculated in the sample solutions by using standard addition method, Then the concentration in µg g^{-1} of each bee honey and edible molasses samples were calculated.

RESULTS AND DISCUSSION

In order to set the optimal condition of the three cations, preliminary measurements were made to obtain the highest peak signal for metal ions Cd(II), Pb(II) and Cu(II) in solution samples. It was noticed that, Briton-Robinson buffer solution (pH ~ 2.1) gave promising results for the determination of Cd, Pb and Cu ions.

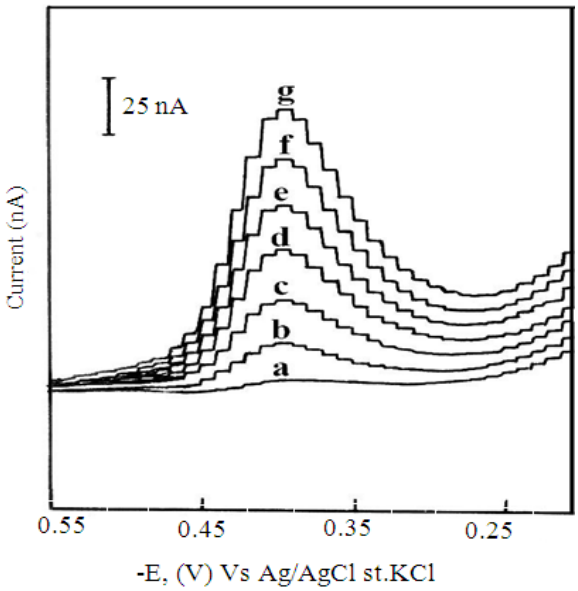

Fig. 1: DPAS Voltammograms of Pb(II) in BC_2 sample in presence of 0.028 M Briton-Robinson buffer solution, pH ~2.1 at deposition potential -0.55 V and different deposition times. (a) zero; (b) 10; (c) 20; (d) 30; (e) 40; (f) 50; (g) 60 sec

The effect of deposition potential of each metal ion was studied and it was observed that the highest and best shape peaks for Cd^{2+}, Pb^{2+} and Cu^{2+} were at deposition potentials -0.75, -0.55 and -0.25 V Vs. Ag/AgCl/ $KCl_{sat.}$ respectively.

The effect of deposition time on the oxidation peak signals of these metal ions was examined. Figure 1 shown differential pulse anodic stripping voltammograms of Pb(II) in BC_2 in buffer solution at different deposition times. The optimal deposition times were selected for these metal ions of all sample solutions in a manner that linear relation must be established between deposition times and current signals and listed in Table 1-3.

DPAS voltammetric determination of Cd(II): Figure 2 represents the differential pulse anodic stripping voltammograms of BC_3 sample solution in absence and in presence of the addition of standard cadmium ions in Briton-Robinson buffer solution of pH ~ 2.1. On plotting of peak current against concentrations for twelve clover honey sample solutions (BC_x) in the same supporting electrolyte at the same conditions, straight lines are obtained (standard addition method) as shown in Fig. 3.

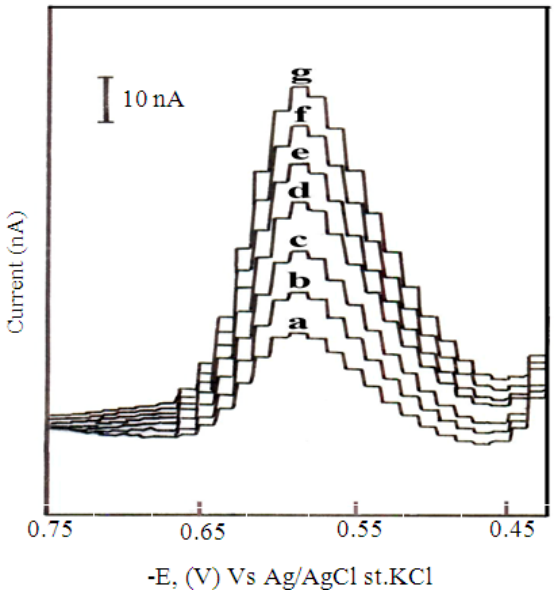

Fig. 2: DPAS Voltammograms of Cd(II) in BC_3 sample spiked with different concentrations of Cd(II) ions in 0.028 M Briton-Robinson buffer solution, pH ~ 2.1 at deposition potential -0.75 V and deposition time 90 sec, (a) sample, S; (b) $S+3\times10^{-9}$; (c) $S+6\times10^{-9}$; (d) $S+9\times10^{-9}$; (e) $S+12\times10^{-9}$; (f) $S+15\times10^{-9}$; (g) $S+18\times10^{-9}$ M Cd(II)

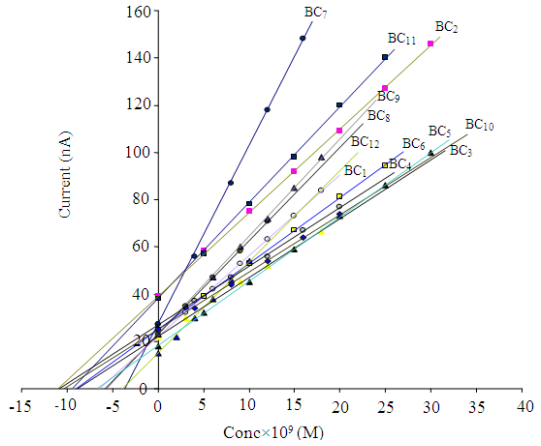

Fig. 3: Standard addition plots of Cd(II) in BC_x samples: (1) BC_1 at 120 sec; (2) BC_2 at 45 sec; (3) BC_3 at 90 sec; (4) BC_4 at 90 sec; (5) BC_5 at 120 sec; (6) BC_6 at 120 sec; (7) BC_7 at 60 sec; (8) BC_8 at 120 sec; (9) BC_9 at 120 sec; (10) BC_{10} at 90 sec; (11) BC_{11} at 30 sec; (12): BC_{12} at 120 sec at deposition potential -0.75 V using (DPASV)

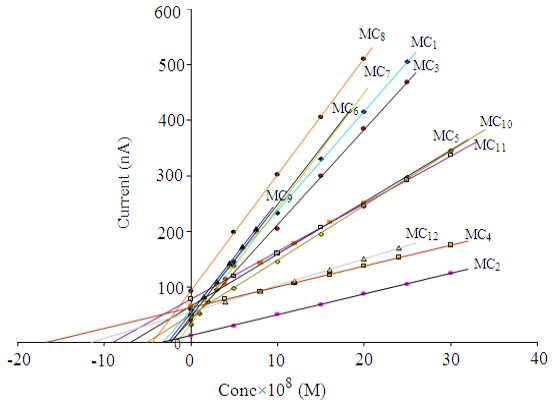

Fig. 4: Standard addition plots of Pb(II) in MC_x Samples: (1) MC_1 at 10 sec; (2): MC_2 at 30 sec; (3) MC_3 at 10 sec, (4) MC_4 at 30 sec; (5) MC_5 at 60 sec; (6) MC_6 at 30 sec; (7) MC_7 at 45 sec; (8) MC8 at 10 sec; (9) MC_9 at 45 sec; (10): MC_{10} at 15 sec; (11) MC_{11} at 15 sec; (12): MC_{12} at 20 sec at deposition potential -0.55 V using (DPASV)

From the interceptions of these lines with the concentration axis at zero current signals, one can calculate the concentration of Cd(II) in each sample. The concentration of Cd(II) ions in all samples (bee honey and edible molasses) under consideration using DPASV are listed in Table 1. The results indicate that, the concentrations of Cd(II) are ranged from 0.001-0.077 μg g^{-1}.

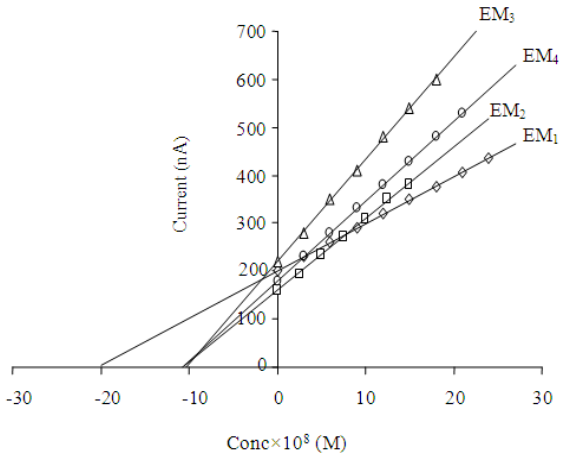

Fig. 5: Standard addition plots of Cu(II) in EM_x samples at deposition potential -0.25 V, using (DPASV): (1) EM_1 at 45 sec; (2) EM_2 at 15 sec; (3) EM_3 at 30 sec; (4) EM_4 at 15 sec

DPAS voltammetric determination of Pb(II): Figure 4 shows the standard addition plots of i.p. against Pb(II) concentration for tweleve multi-flower honey sample solutions (MCx) in Briton-Robinson buffer solution of pH ~ 2.1 at deposition potential -0.55 volt. From the interceptions of these straight lines with the concentration axis at zero current signal, the concentration of Pb(II) ions in all samples (bee honey and edible molasses) under consideration using DPASV was calculated and the resulting concentration values are listed in Table 2. The results indicate that, the concentration of Pb(II) ions are ranged from 0.006-1.640 μg g^{-1}

DPAS voltammetric determination of Cu(II): Figure 5 shows the standard addition plots of ip against Cu(II) concentration for four edible molasses sample solutions (EM_x) in Briton-Robinson buffer solution of pH ~ 2.1 at deposition potential -0.25 volt. From the interceptions of these straight lines with the concentration axis at zero current signal gives the concentration of Cu(II) in the voltammetric cell for each sample. After correction for the background current of blank experiments. The concentration of Cu(II) ions in all samples (bee honey and edible molasses) under consideration using DPASV are shown in Table 3. It was found that, the mean levels of Cu(II) ions are ranged from 0.085-0.987 μg g^{-1}.

The precision and reproducibility of the selected procedurewere investigated by measuring the concentration of Cd(II), Pb(II) and Cu(II) in all bee honey and edible molasses samples under consideration for (n = 5).

Table 2: Lead content of different clover (BC_x), multi-flower (MC_x) citrus (OC_x) honey samples and edible molasses samples (EM_x) (a mean value ± standard deviation for n = 5 at the 95% confidence level)

Samples number	T_d (sec)	Lead content (mean ± SD) μg g^{-1}	Regression parameter: Correction coefficient	Confidence: Higher	Confidence: Lower	Cadmium content (mean ± SD) μg g^{-1} (GFAAS)
BC_1	20	1.640±0.081	0.9995	1.741	1.539	1.650±0.112
BC_2	40	0.616±0.021	0.9993	0.642	0.589	0.618±0.014
BC_3	30	1.060±0.062	0.9996	1.138	0.984	1.080±0.102
BC_4	30	0.595±0.043	0.9995	0.645	0.545	0.586±0.031
BC_5	45	0.124±0.011	1.0000	0.138	0.110	0.117±0.008
BC_6	60	0.093±0.009	1.0000	0.104	0.082	0.095±0.007
BC_7	30	1.521±0.042	0.9992	1.573	1.469	1.590±0.172
BC_8	60	0.263±0.032	0.9990	0.303	0.223	0.270±0.019
BC_9	20	0.507±0.011	0.9990	0.521	0.493	0.520±0.018
BC_{10}	45	0.692±0.081	0.9992	0.792	0.591	0.695±0.063
BC_{11}	10	0.521±0.022	0.9991	0.547	0.492	0.529±0.012
BC_{12}	30	0.187±0.013	0.9999	0.203	0.171	0.195±0.014
MC_1	10	0.261±0.022	0.9997	0.287	0.233	0.262±0.021
MC_2	30	0.267±0.044	0.9997	0.322	0.212	0.272±0.032
MC_3	10	0.130±0.011	0.9993	0.143	0.117	0.137±0.015
MC_4	30	1.610±0.121	0.9994	1.762	1.462	1.624±0.202
MC_5	60	0.702±0.081	0.9992	0.802	0.601	0.692±0.041
MC_6	30	0.178±0.006	0.9998	0.186	0.171	0.176±0.034
MC_7	45	0.087±0.003	0.9993	0.091	0.083	0.095±0.006
MC_8	10	0.404±0.022	0.9993	0.431	0.377	0.419±0.018
MC_9	45	0.200±0.013	0.9993	0.216	0.184	0.207±0.012
MC_{10}	15	0.438±0.081	0.9992	0.539	0.337	0.450±0.032
MC_{11}	15	0.806±0.054	0.9993	0.873	0.739	0.823±0.018
MC_{12}	20	1.065±0.104	0.9992	1.194	0.936	1.078±0.123
OC_1	40	0.101±0.011	0.9992	0.115	0.087	0.100±0.002
OC_2	40	0.324±0.021	0.9995	0.351	0.298	0.337±0.019
EM_1	60	0.006±0.001	0.9994	0.007	0.005	0.007±0.001
EM_2	45	0.051±0.004	0.9994	0.056	0.046	0.053±0.004
EM_3	45	0.138±0.005	0.9994	0.144	0.132	0.141±0.011
EM_4	45	0.201±0.011	0.9991	0.215	0.187	0.209±0.015

The values of slopes, intercepts, confidence intervals, standard deviations and correlation coefficient obtained for all samples are listed in Table 1-3. These statistical parameter values indicate the reproducibility of the procedure for determination of each Cd(II), Pb(II) and Cu(II) in all samples in this Briton-Robinson buffer solution, PH ~ 2.1.

Flame atomic absorption spectrometric determination of copper: Copper was determined by atomic absorption spectroscopy of the treated sample solutions at 324.7 nm. The concentration values of each sample are listed in Table 3. It was found that the concentration of copper is ranged between 0.077-0.991 μg g^{-1}. From Table 3 it was found that, the data obtained by stripping voltammetry are in a close agreement with those obtained by flame atomic absorption spectrometry. Flame atomic absorption spectrometric method was not obeyed for determination of cadmium and lead, so the concentration of each cadmium and lead is less than the detection limits of the FAAS technique.

Graphite furnace atomic absorption spectrometric determination of cadmium and lead: Cadmium and lead were determined by graphite furnace atomic absorption spectrometry at 228.9 and 283.2 nm respectively. The resulting data of cadmium and lead were listed in Table 1 and 2 respectively. From Table 1 and 2, it was found that, the resulting data obtained by stripping voltammetry are in a close agreement with those obtained by graphite furnace atomic absorption spectrometry.

The foregoing results indicated that, copper, cadmium and lead contents in the bee honey and edible molasses samples are less than that permissible values which given by WHO and FAO and differ from each other's according to its botanical sources (only in case of bee honey), environment contamination, production and storage.

Table 3: Copper content of different clover (BC_x), multi-flower (MC_x) and citrus (OC_x) honey samples and edible molasses samples (EM_x) (a mean value ± standard deviation for n = 5 at the 95% confidence level)

Samples number	T_d (sec)	Copper content (mean ± SD) μg g^{-1}	Regression parameter: Correction coefficient	Confidence: Higher	Confidence: Lower	Cadmium content (mean ± SD) μg g^{-1} (GFAAS)
BC_1	40	0.497±0.052	0.9996	0.559	0.435	0.503±0.011
BC_2	30	0.230±0.013	0.9994	0.242	0.218	0.238±0.021
BC_3	45	0.242±0.021	0.9994	0.267	0.217	0.252±0.009
BC_4	20	0.242±0.012	0.9995	0.257	0.227	0.239±0.013
BC_5	30	0.696±0.091	0.9997	0.809	0.583	0.701±0.042
BC_6	30	0.300±0.012	0.9994	0.315	0.285	0.292±0.024
BC_7	45	0.193±0.009	0.9998	0.204	0.182	0.189±0.018
BC_8	30	0.220±0.023	0.9992	0.248	0.191	0.225±0.012
BC_9	45	0.286±0.013	0.9993	0.302	0.269	0.287±0.017
BC_{10}	40	0.504±0.014	0.9993	0.521	0.487	0.512±0.031
BC_{11}	10	0.747±0.051	0.9994	0.811	0.684	0.734±0.019
BC_{12}	30	0.308±0.008	0.9995	0.318	0.298	0.301±0.024
MC_1	15	0.987±0.121	0.9992	1.137	0.837	0.991±0.051
MC_2	30	0.255±0.023	0.9993	0.284	0.226	0.251±0.022
MC_3	10	0.085±0.012	0.9995	0.099	0.071	0.077±0.004
MC_4	30	0.165±0.013	0.9991	0.181	0.149	0.177±0.021
MC_5	15	0.171±0.032	0.9996	0.211	0.131	0.174±0.023
MC_6	15	0.813±0.093	0.9994	0.927	0.697	0.828±0.061
MC_7	30	0.398±0.041	0.9997	0.449	0.347	0.407±0.015
MC_8	10	0.555±0.014	0.9992	0.572	0.538	0.552±0.023
MC_9	30	0.512±0.082	0.9996	0.614	0.411	0.525±0.051
MC_{10}	45	0.161±0.013	0.9993	0.177	0.145	0.158±0.011
MC_{11}	20	0.335±0.021	0.9997	0.361	0.309	0.335±0.043
MC_{12}	30	0.303±0.013	0.9993	0.319	0.287	0.300±0.017
OC_1	30	0.393±0.032	0.9991	0.433	0.353	0.401±0.009
OC_2	45	0.275±0.013	0.9998	0.291	0.259	0.292±0.013
EM_1	45	0.646±0.033	0.9996	0.687	0.605	0.656±0.021
EM_2	15	0.309±0.011	0.9990	0.323	0.295	0.323±0.012
EM_3	30	0.301±0.013	0.9995	0.317	0.285	0.298±0.012
EM_4	15	0.315±0.009	1.0000	0.326	0.304	0.322±0.016

CONCLUSION

The use of Briton-Robinson buffer solution after a wet digestion method for determination of Cd(II), Pb(II) and Cu(II) ions by differential pulse anodic stripping voltammetry is selected method for determination of these metal ions in bee honey and edible molasses samples. This procedure presented a better detection limit than others, which reported in the literature. This method is also allowed Cd, Pb and Cu determination in the same voltammetric cell without external addition of base to change the pH value. The time of determination is shorter than that by other methods. From the foregoing results, one can concluded that, the application of standard addition method for anodic stripping voltammetric determination of divalent cadmium, lead and copper in honey samples as well as in edible molasses samples is suitable and successful.

REFERENCES

Ajtony, Z., L. Bencs, R. Haraszi, J. Szigeti and N. Szoboszlai, 2007. Study on the simultaneous determination of some essential and toxic trace elements in honey by multi-element graphite furnace atomic absorption spectrometry. Talanta, 71: 683-690.

Antonescu, C. and C. Mateescu, 2001. Environmental pollution and its effects on honey quality. Roman. Biotechnol. Lett., 6: 371-379.

Batuman, V., J.K. Maesaka, B. Haddad, E.Tepper and E. Landy *et al*., 1981. The role of lead in gout nephropathy. N. Engl. J. Med., 304: 520-523.

Bogdanov, S., A. Imdorf, J.D. Charriere, P. Fluri and V. Kilchenmann, 2003. The Contaminants of the bee Colony. Swiss Bee Research Center, Bern, Switzerland. http://hirschbachapiary.com/Documents/The%20contaminants%20of%20the%20bee%20colony.pdf

Bogdanov, S., V. Kilchenmann and P. Fluri, U. Buhler and P. Lavanchy, 1999. Influence of organic acids and components of essential oils on honey taste. Am. Bee J., 139: 61-63.

Buldini, P.L., S. Cavalli, A. Mevoli and J.L. Sharma, 2001. Ion chromatographic and voltammetric determination of heavy and transition metals in honey. Food Chem., 73: 487-495.

Caroli, S., G. Forte, A.L. Iamiceli and B. Galoppi, 1999. Determination of essential and potentially toxic trace elements in honey by inductively coupled plasma-based techniques. Talanta, 50: 327-336.

Clarkson, T.W., 1988. Biological Monitoring of Toxic Metals. 1st Edn., Plenum Press, USA., ISBN-10: 0306428091, pp: 686.

Dadant and Sons, 1992. The Hive and the Honey Bee. Dadant and Sons, Hamilton, Illinois, USA., ISBN: 10: 0915698099, pp: 1324.

Ensafi, A.A., T. Khayamian and S.S. Khaloo, 2004. Application of adsorptive cathodic differential pulse stripping method for simultaneous determination of copper and molybdenum using pyrogallol red. Anal. Chim. Acta, 505: 201-207.

Fernandez, M.C., E. Subra and A. Ortiz, 1994 Honey, environmental indicator. Environmental practices for quality agriculture. Proceeding of the Congress of the Spanish Society of Organic Agriculture, (SSOA'94) Toledo, Spain, pp: 37-44.

Fernandez-Torres, R., J.L. Perez-Bernal, M.A. Bello-Lopez, M. Callejon-Mochon, J.C. Jimenez-Sanchez and A. Guiraum-Perez, 2005. Mineral content and botanical origin of Spanish honeys. Talanta, 65: 686-691.

Fredes, C. and G. Montenegro, 2006. Heavy metals and other trace elements contents in Chilean honey. Cien. Inv. Agric., 33: 50-58.

Ioannidou, M.D., G.A. Zachariadis, A.N. Anthemidis and J.A. Stratis, 2005. Direct determination of toxic trace metals in honey and sugars using inductively coupled plasma atomic emission spectrometry. Talanta, 65: 92-97.

Kump, P., M. Necemer and J. Snajder, 1996. Determination of trace elements in bee honey, pollen and tissue by total reflection and radioisotope X-ray fluorescence spectrometry. Spectrochim. Acta Part B: Atomic Spectrosc., 51: 499-507.

Lachman, J., D. Kolihova, D. Miholova, J. Kosata, D. Titera and K. Kult, 2007. Analysis of minority honey components: Possible use for the evaluation of honey quality. Food Chem., 101: 973-979.

Li, Y., F. Wahdat and R. Neeb, 1995. Digestion-free determination of heavy metals (Pb, Cd, Cu) in honey using anodic stripping differential pulse voltammetry and potentiometric stripping analysis. Fresenius J. Anal. Chem., 351: 678-682.

Lide, D.R., 2005. CRC Handbook of Chemistry and Physics. CRC, 86th Edn., Florence, Kentucky, USA., ISBN-13: 9780849304866, pp: 2544.

Munoz, E. and S. Palmero, 2006. Determination of heavy metals in honey by potentiometric stripping analysis and using a continuous flow methodology. Food Chem., 94: 478-483.

Packer, A.P. and M.F. Gine, 2001. Analysis of undigested honey samples by isotope dilution inductively coupled plasma mass spectrometry with direct injection nebulization (ID-ICP-MS). Spectrochim. Acta Part B, 56: 69-75.

Rodriguez-Garcia, J.C., J. Barciela-Garcia, C. Herrero-Latorre, M. Freire-Rodriguez, S. Garcia-Martin and R.M. Pena-Crecente, 2003. Comparison of palladium-magnesium nitrate and ammonium dihydrogenphosphate modifiers for cadmium determination in honey samples by electrothermal atomic absorption spectrometry. Talanta, 61: 509-517.

Sanna, G., M. Pilo, P.C. Piu, A. Tapparo and R. Seeber, 2000. Determination of heavy metals in honey by anodic stripping voltammetr at microelectrodes. Anal. Chim, Acta, 415: 165-173.

Simon, J.A. and E.S. Hudes, 1999. Relationship of ascorbic acid to blood lead levels. J. Am. Med. Assoc., 281: 2289-2293.

Taddia, M., A. Musiani and S. Schiavi, 2004. Determination of heavy metals in honey by Zeeman electrothermal atomic absorption spectrometry. Ann. di Chim., 94: 107-111.

Terrab, A., A.F. Recamales, M.L. González-Miret and F.J. Heredia, 2005. Contribution to the study of avocado honeys by their mineral contents using inductively coupled plasma optical emission spectrometry. Food Chem., 92: 305-309.

Tuzen, M. and M. Soylak, 2005. Trace heavy metal levels in microwave digested honey samples from middle Anatolia, Turkey. J. Food Drug Anal., 13: 343-347.

Vinas P., I. Lipez-Garcia, M. Lanzon and M. Hernandez-Cordoba, 1997. Direct determination of lead, cadmium, zinc, and copper in honey by electrothermal atomic absorption spectrometry using hydrogen peroxide as a matrix modifier. Agric. Food Chem., 45: 3952-3956.

Vogel, A.I. and J. Basset, 1978. A Textbook of Quantitative Inorganic Analysis. 4th Edn., Longman, London, pp: 925.

Wilson, L.D., 1998. Nutritional Balancing and Hair Mineral Analysis. Lawrance Wilson, ISBN: 10: 0962865745, pp: 389.

Yilmaz, H. and O. Yavuz, 1999. Content of some trace metals in honey from south-eastern Anatolia. Food Chem., 65: 475-476.