Závěrečná zpráva projektu specifického výzkumu - zakázka č. 2111

Název projektu: Vliv zpracování medu na obsah těžkých kovů

Specifikace řešitelského týmu

Odpovědný řešitel: doc. RNDr. Vlastimil Dohnal, Ph.D. et Ph.D.

Studenti doktorského studia na PdF UHK: ne

Studenti magisterského studia na PřF UHK: Bc. Luděk Janata

Další výzkumní pracovníci:

Celková částka přidělené dotace: 156 952 Kč

Stručný popis postupu při řešení projektu

Mezi významné kontaminanty ŽP patří těžké kovy. Mezi nejvýznamnější zdroje patří skládky, průmyslové výroby, spalovací procesy a průmyslová hnojiva. Těžké kovy nejsou v životním prostředí degradovány, proto dochází k jejich kumulaci v jeho jednotlivých složkách. Následně se stávají součástí potravního řetězce, kde působí toxicky. Mechanismus toxického působení se u jednotlivých kovů liší, společným cílem jejich působení jsou často ledviny či játra.

Včela a její produkty jsou též vhodnými bioindikátorem stavu ŽP, protože včela se pohybuje v omezené vzdálenosti od úlu. Dle dostupnosti potravy jsou to řádově stovky metrů až 6-8 km.

Včela medonosná se dostává do kontaktu téměř se všemi složkami životního prostředí (ŽP). Je producentem medu, vosku, propolisu a dalších produktů, ve kterých se odráží kvalita ŽP. Z tohoto důvodu se považují tyto produkty včetně včel samotných za významné bioindikátory jeho stavu. Mezi významné kontaminanty v medu patří i těžké kovy, zejména pak Cu, Fe, Mn, Ni a Zn. K další kontaminaci může docházet při jeho zpracování případným přechodem těchto prvků z medometů.

Kontrolou medu před uvedením na trh se zabývá Odbor hygieny a kontroly veřejného zdraví Státní veterinární správy, v obchodní síti pak Státní zemědělská a potravinářská inspekce. V českém medu nebyla zaznamenána zdravotně závadná koncentrace těžkých kovů. Tato skutečnost se týká pouze medu uváděného na trh, nikoliv medu určeného pro samospotřebu. Na tuto významnou oblast producentů je zaměřen tento projekt, v jehož rámci bude zkoumán vliv použitého zařízení (medometu) na obsah těžkých kovů v medu. Společně s tímto experimentem dojde ke stanovení obsahu těžkých kovů v tělech včel a výsledky budou porovnány s podobnými studiemi realizovanými v České republice a v zahraničí.

Metodika řešení

Vzorky medu byly získávány dvěma způsoby – samovolným vytečením medu z plástve (kontrolní vzorek) a vytočením medu na medometu. V rámci pokusu byly testovány 3 druhy rámečků. Vzorky byly uchovávány v plastových nádobách předem vymytých zředěnou kyselinou dusičnou, aby se zabránilo jejich dodatečné kontaminaci. Med byl následně mineralizován v muflové peci (oproti plánu část vzorků byla pro porovnání mineralizována v mikrovlnném reaktoru) a poté obsah těžkých kovů změřen metodou atomové absorpční spektroskopie a metodou indukčně vázaného plazmatu na pracovišti ve Vídni (Institute for Technical Chemistry and Analytics, Vienna University of Technology).

V případě vzorků těl včel byla sbírána uhynulá těla včel, která byla analyzována stejným způsobem. Výsledky jejich analýz byly silně ovlivněny kontaminací vzniklé při jejich sběru, proto tyto výsledky nemohly být použity.

Původní časový plán řešení projektu se nepodařilo dodržet. Nákupy potřebného materiálu plánované na květen byly realizovány až v říjnu 2013, což řešení celé práce velmi zdrželo a zkomplikovalo. Lze však pozorovat jisté zlepšení, neboť v roce 2012 se nepodařilo zakoupit z požadovaných drobných laboratorních přístrojů vůbec nic.

Splnění kontrolovatelných výsledků řešení

Část výsledků získaných při řešení projektu je shrnuta v přiloženém rukopisu publikace, který bude po korekci rakouské strany odeslán do časopisu s IF tematicky zaměřeného na analytickou chemii potravin respektive toxikologii. Zbytek výsledků bude využit při další práci.

Do OBD nebyl zadán žádný záznam.

Navíc oproti plánu bude část výsledků projektu prezentována na mezinárodní konferenci ESAS 2014 konané v Praze.

Zároveň dojde k obhajobě diplomová práce na toto téma od participujícího studenta.

Tab. 1 Sumář výstupů řešení projektu

Typ výstupu	**Plán**	**Skutečnost**	**Poznámka (např. vyšlo, přijato, v redakčním řízení apod.**
Počet dizertačních prací			
Počet diplomových prací	1	1	obhajoba 2014
Zařazeno do kategorie excelence			
Jimp - výstup v impaktovaném časopisu	1	1	Před odesláním
J - ostatní odborná periodika			
B - odborná kniha			
C - kapitola v odborné knize			
D - článek ve sborníku	0	1	ESAS 2014
F - užitný vzor aj.			
Počet výsledků celkem	2	3	

Tab. 2 Čerpání finančních prostředků v Kč

Položka	**Plán**	**Žádost o změnu rozpočtu**	**Skutečnost**
Počet členů řešitelského týmu čerpajících mzdové prostředky	1		1
Počet studentů čerpajících mzdové prostředky	1		1
Stipendia	6 000		6 000
Odměny a DPP, DPC	2 600		2 602
Zákonné zdravotní a sociální pojištění	1 365		1 364
Celkem osobní náklady	9 965		9 965
Spotřeba materiálu celkem	46 287		47 591
Drobný hmotný majetek	100 700		98 172,00
Služby celkem	0		0
Cestovné celkem	0		0
Celkové náklady	156 952		157 092

Datum: 6.1.2014

Podpis odpovědného řešitele

Příloha 1a. Rukopis článku k zaslání pro recenzní řízení pro časopis s IF

Příloha 1b. Abstrakt přihlášený na konferenci ESAS 2014

Příloha 2. výpis z OBD - výsledky publikační činnosti podpořené projektem

Příloha 3. Výsledovka z Magionu – vyúčtování dotace

Příloha 1a: Rukopis článku k zaslání pro recenzní řízení pro časopis s IF

INFLUENCE OF HONEY PROCESSING ON HEAVY METAL CONTENT

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ABSTRACT

Heavy metals are cumulative toxic compounds which longtime exposition may lead to serious negative health effects. One of their dietary sources is honey. This work deals with investigation of influence of honey production process on heavy metals content in final product. The honey was evaluated in two stages of process: at the beginning of the process, when the honey flows freely from uncapped frames and after extraction. There were tested two the most common extractors. The first of them, older one, was made of tinplate. The components were connected by solder consisting mainly of tin and lead. The second extractor was made of stainless steel. The results shows, that the process of honey extraction does not affect content of heavy metals in honey.

KEYWORDS

Honey, heavy metals, honey extraction

INTRODUCTION

Honeybees *Apis mellifera* and their product honey are considered as the bioindicators associated with environmental quality. Honeybees are in contact with various environmental pollutants due to theirs intense foraging activity. The pollution can affect them and their products such as honey, propolis etc. Also, the use of bees as bioindicators allows monitoring of relatively small area. Depending on the food abundance the radius of their activity varies from a few hundred meters to several kilometers from the hive.

Several enzymes and metabolites of honeybees were evaluated as a biomarker of environmental pollution by pesticides, neurotoxic compounds or heavy metals. Phase-II enzyme glutathione-S-transferase (GST) conjugating xenobiotics with glutathione, alkaline phosphatase (ALP) as the non-specific biomarkers, acetylcholinesterase (AChE) for neurotoxic compounds such as pesticides monitoring and metallothioneins (MT) as metal chelating agents were used for environmental quality evaluation (Badiou-Bénéteau, 2013). Same authors used determination of GST, carboxylesterases (CaE1 and CaE2), both are involved in detoxification processes, AChE and catalase activity as a biomarker of exposure to xenobiotics (Badiou-Bénéteau, 2012).

Honey is a sweet substance produced by bees from the nectar of flowers and/or secretes of plants or insects (honeydew). The main components of honey are saccharides such as glucose, fructose and saccharose, followed by water, proteins, enzymes, pollen, wax, minerals, aromatic oils etc. The content of minerals in honey is relatively very low. It ranges from approximately 0.1 to 0.2 %. The main source of metals is environment such as dust, pollen, soil, water, air, nectar etc. where the honey is produced. Various studies and reviews were published that focused on relationship between metal content in honey and environmental pollution.

Heavy metals may come from external sources such as industrial smelter pollution, factory emissions, non-ferrous metallurgy, leaded petrol from busy highways, incorrect procedures during honey processing and conservation phases, as well as agrochemicals such as cadmium-contaminated fertilizers, organic mercury and arsenic-based pesticides still used in some countries. Especially, the unprotected metal surfaces of processing instruments can be rich sources of iron (Merin et al., 1998). Heavy metals can cumulate in human organism and during long term exposition their concentration can overcome toxic level.

Various analytical methods were employed in heavy metals determination. The most preferred are atomic spectroscopic methods such as flame or electrothermal atomization atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma or ICP in combination with optical emission analysis (Batista et al., 2012) or mass spectrometric detection. Also, electrochemical methods such as potentiometry (Muñoz and Palmero, 2006) and voltammetry (Sanna et al., 2000) were applied.

Atomic absorption spectrometry is the most used analytical techniques for determination of heavy metal content in honey. Two approaches for sample treatment are applied in honey analysis. The first one uses direct analysis of samples without previous mineralization. Honey samples are diluted with solution of nitric acid and directly introduced into nebulizer and acetylene-air flame (Hernández et al., 2005). When electrothermal atomization is used, sample is diluted with solution of nitric acid and hydrogen peroxide and mineralized/atomized in graphite furnace (Andrade, 2014; Tuzen et al., 2007). The second approach involves different methods of digestion of honey samples including dry ashing or with several chemicals, ultrasonication, microwave assisted digestion and UV photolysis (Andrade, 2014).

MATERIALS AND METHODS

SAMPLES

All the material used was made of plastic and before use all pieces were thoroughly washed with 5% nitric acid. Bees were kept in plastic and wooden hives filled with frames with/without grid.

Honey samples were obtained from honey keepers of Hradec Králové region and Moravian-Silesian region of Czech Republic, subject to different treatment in the honey making process.

RAW HONEY

Three variants of frames were used – frame without grid, frame with plastic grid and frame with steel grid. When frames were completely filled with honey, they were removed from supers (the box with frames in hive), part of the frame was uncapped using sharp plastic knife and honey was collected and stored. Honey from this processing step was collected. Uncapped frames were inserted to extractor and honey centrifuged out of the frames.

EXTRACTED HONEY

Two models of extractor were used. The first of them, older one, was made of galvanized sheets. The components were connected by solder consisting mainly of tin and lead. The second extractor was made of stainless steel. Samples of extracted honey were collected and stored in plastic sample tubes previously washed with 5% nitric acid.

Twenty-seven samples were analyzed (3 samples of raw honey, 3 types of frames (without and with plastic/steel grid) and 2 extractors, each sample in three repetitions) (Figure 1).

SAMPLE PREPARATION

MUFFLE FURNACE

Prior analysis, the honey samples were heated to 40 °C in water bath (JULABO MB-5, Julabo Labortechnik GMBH, Seelbach, Germany). Approximately 10 g of sample was weighted to quartz crucible on Kern ABS 120-4 balances (Kern and Sohn, Balingen, Germany). Then, crucibles were capped and slowly and gently heated on the stove (model ETA 2107, Hlinsko, Czech Republic) to remove water. Then crucibles were placed at muffle furnace model MSK 030 (MAT, spol. s.r.o., Ostrava, Czech Republic). Muffle furnace program was set to following parameters: warm up (60 °C/h) and heating at constant temperature 120 °C for 3 hours, heating ramp of 8 hours to 600 °C and heating for 8 hours. Samples were taken out of the furnace after cooling to laboratory temperature. The mineralization program is shown on Fig. 2.

After mineralization, dry-ashed samples did not exhibit any substantial residues of the organic honey matrix matter (white ash and clear solutions). All sampling vessels were thoroughly rinsed and diluted with 1% HNO3 to 25 mL of total sample volume for instrumental analyses.

METAL STANDARDS

All the standards ASTASOL® were obtained from Analytika, s.r.o. (Prague, Czech Republic) as solutions with certified concentrations 1.000 +- 0.005 g/l at 20 °C in 2% nitric acid. Standards of Cd, Pb and Cu were prepared from metals of purity 99.999 %, Zn, Fe from metals of purity 99.995 %, Ni from metal of purity 99.99 % and Cr from chromium nitrite nonahydrate 99.99 %.

SAMPLE ANALYSIS

Mineralized samples were analyzed by flame atomic absorption spectrometry (model AAnalyst 400, Perkin Elmer, Waltham, Massachusetts, USA). The flame composed of acetylene (Acetylene 2.6, SIAD, Braňany, Czech Republic) and compressed air (model DK50 PLUS, EKOM, Piešťany, Slovakia). Data were collected and evaluated by software WinLab 32 AA by Perkin Elmer (Waltham, Massachusetts, USA).

RESULTS AND DISCUSSION – CD, CR, CU, FE

As reported in review of Pohl (2009), the content of metals is influenced by geographical and botanical origin and processing. Our work was focused on the first two steps of the process (Figure 3 – adapted from Pohl, 2009).

There were supposed higher concentration of lead and zinc in samples extracted with old extractors. The results showed, that content of these metals is very low and after extraction it still remains under the limits of detection. The concentrations of Zn, Ni and Pb were under limit of detection, therefore there can´t be evaluated the influence of honey processing. The content of Cd, Cr, Cu respective Fe obtained for studied samples are presented in Table 1.

Cd

The main sources of cadmium exposure in human are tobacco products, followed by diet. Cadmium may probably play role in human carcinogenesis. Thus, there is a necessity to monitor Cd concentration in food samples (WHO, 2004). Due to its half-life in human body (10-30 years) the European Food Safety Authority set tolerable weekly intake (TWI) to 2.5 μg/kg b.w.week (EFSA, 2009). Cadmium ions Cd(II) are absorbed by plant roots and then easily transported in the form of metallothioneins to various parts of plants including nectar. Also, it co-occurs with lead and zinc in theirs ores and alloys.

Typical concentrations of Cd in honey are in ones of μg/kg. For example, Ru et al. (2013) found concentration 1.34 μg/kg of Chinese honey, Andrade et al. (2014) <2.0-8 μg/kg of honey from region Paraná (Brazil). Przybyłowski et al. (2001) analysed various kinds of Polish honey and found cadmium concentrations 8-27 μg/kg. Very low content of Cd, 0.9-17.9 μg/kg, was determined by Tuzen (2007) in Turkish honeys of different botanical origin. Relatively high concentrations, up to 450 μg/kg, were found in New Zealand monofloral honey samples (Vanhanen et al., 2011).

Our results showed, that cadmium content in samples was between 3.5 and 4.2 μg/kg and didn't show any trends towards the way of processing. Geographic influences seem to be more important.

Cr

Chrome ions were detected in ones to hundreds of μg/kg of honey. For example 2.4-37.6 μg/kg (Tuzen, 2007), 83-94 μg/kg (Andrade, 2014), 430 μg/kg (Vanhanen, 2011). The toxicity of chrome ions strongly depends on oxidation state. While toxicity of trivalent chrome Cr(III) is relatively low, hexavalent chrome Cr(VI) is cancerogenic. Chrome (VI) is typical product of anthropogenic activity (Bartlett et al., 1988). The WHO considered that supplementation of chrome (III) in adults should not exceed 250 μg/day. In our study the oxidation state was not investigated and the chrome concentration was determined as a total content.

Our results showed, that concentration of chrome increased with use of stainless steel extractor. This increase can be caused by the material – because depending on grade/intended use, stainless steel can contain 12-30% of added chrome.

Cu

Copper is biogenic metal and it is frequently presented in redox metalloenzymes. Apparently, mines and steelworks, industrial and urban areas or highways can results in an increase of certain metals, such as Cd and Cu. Also, beekeepers and their tools and equipment can contaminate processed honey (Pohl, 2009). Joint FAO/WHO Expert Committee on Food Additives (JECFA) estimated provisional maximum tolerable daily intake for man (PMTDI) 0.05-0.5 mg/kg b.w. day.

Typical concentrations of Cu in honey samples are in ones to thousands of μg/kg of honey. Ru et al. (2013) found 46.18 μg/kg, Badiou-Bénéteau (2013) 226-240 μg/kg in honey samples from island Réunion, Vanhanen (2011) n.d.-250 μg/kg and Tuzen (2007) 230-2410 μg/kg (in honey samples from different botanical origin, collected all over the Turkey. Our samples contained approximately 50-70 μg/kg of copper, independent of extractor material.

Fe

The main sources of iron are environmental (soil, dust etc.) and processing origin. The acidity of honey promotes corrosion, wear and dissolution of beekeepers tools and equipments and storage metal containers. The content of iron influences the sensory properties of honey. Higher concentration of iron may lead to so called tar-black tea effect (Merin, 1998). JECFA set PMTDI to 0.8 mg/kg b.w.day, for all sources except for iron oxide colouring agents, supplemental iron for pregnancy and lactation, and supplemental iron for specific clinical requirements.

The concentration of iron in honey samples varies between hundreds to several thousands μg/kg. For example, 670-2710 μg /kg (Vanhanen, 2011), 1150-1201 μg /kg (Badiou-Bénéteau, 2013), 1800-10200 μg /kg (Tuzen, 2007).

Our results showed,iron concentration around 700 μg /kg of honey. The iron concentration was elevated in samples that were processed in stainless steel extractors and unchanged in samples from the old-type extractor from galvanized sheet metal.

Based on SISP04 database, only 6.3 % (men 18-59 years) -14.0 % (children 4-6 years old) consume honey with average dose 0.30 g/b.w.day respective 0.93 g/b.w.day. Overall consumption of honey in Czech population varies between 0.019 and 0.120 g/b.w.day (Ruprich et al., 2006). For all metals determined in our study there were not observed amounts that could not significantly contribute to their intake in diet of typical composition.

CONCLUSIONS

The influence of extraction process on selected metal content in honey was evaluated. Two kinds of honey extractor were evaluated. The first of them was made of tinplate. The components were connected by solder consisting mainly of tin and lead. The second extractor was made of stainless steel. Our results showed, that the concentration of cadmium and copper were unaffected. The content of iron and chrome in processed honey was slightly higher when the stainless steel extractor was used. The influence of galvanized sheet extractor couldn't be quantified as its typical elements' concentrations were lower than limit of detection. On the other hand, the overall concentration of monitored elements are very low and environmental sources and influences seem to play much more important role in transport of the metal species into honey during its production in the hives than physico-chemical processes during its contact with extractors. Determined overall contents for monitored metals are in agreement with previously published results by other groups. Based on honey consumption data for Czech Republic, the levels of all determined metals are much lower than their recommended intake limits. Thus, the consumption of tested honey does not have significant toxicological relevance.

ACKNOWLEDGEMENT

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TABLES

Table 1: Concentrations of selected metals in honey during honey processing. All measurements were repeated 3 times. Values are in μg/kg.

Sample of HK region	Cd		Cu		Cr		Fe	
	average	RSD	average	RSD	average	RSD	average	RSD
Raw honey	3,74 ± 0,13	3,36%	50,22 ± 1,97	3,93%	24,04 ± 1,41	5,87%	495.48 ± 16.19	3.27%
Galvanized sheet extractor	3,71 ± 0,17	4,41%	51,04 ± 1,04	2,04%	23,59 ± 1,37	5,80%	533,45 ± 13.77	2,58%
Stainless steel extractor	3,58 ± 0,17	4,79%	52,73 ± 1,04	2,71%	34,44 ± 1,34	3,90%	747,32 ± 10,37	1.39%

Sample of M-S region	Cd		Cu		Cr		Fe	
	average	RSD	average	RSD	average	RSD	average	RSD
Raw honey	4,03 ± 0,18	4,37%	68,21 ± 3,54	5,19%	30,93 ± 1,01	3,25%	602,18 ± 16,69	2,77%
Galvanized sheet extractor	------	------	------	------	------	------	------	------
Stainless steel extractor	4,15 ± 0,19	4,52%	67,38 ± 4,06	6,02%	46,05 ± 1,83	3,98%	786,08 ± 16,41	2,09%

FIGURES

Figure 1.: Process of honey samples preparation

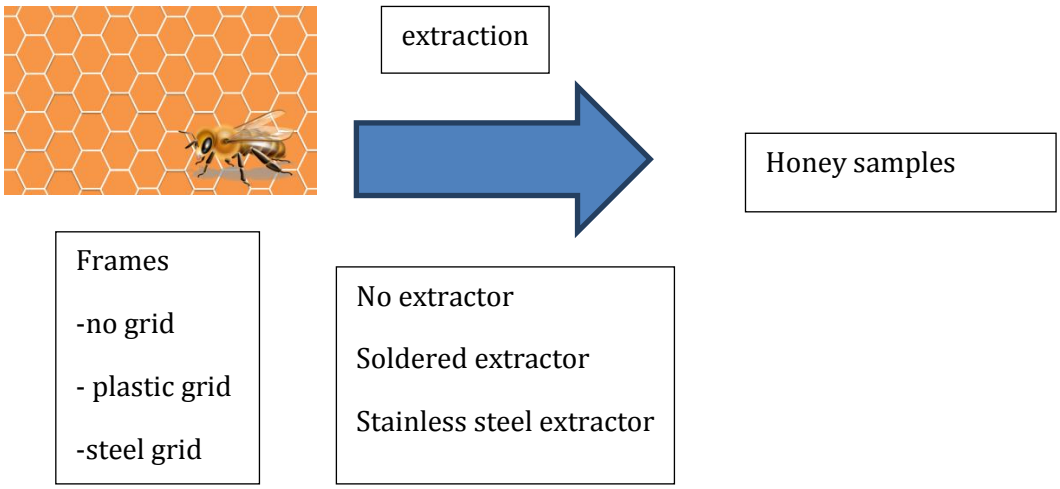

Figure 2: Furnace ashing program

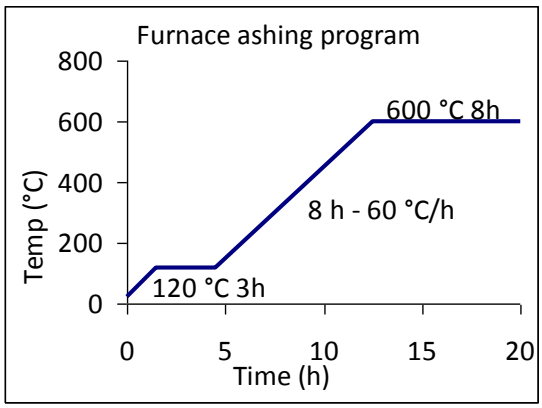

Figure 3. Contamination sources in various honey processing stages

Processing stage	**Contamination sources**
Super and frames removal	Hive paints and preservatives, soil, plant materials, environment
↓	
Uncapping and extraction	De-capping equipment, extractors, containers (holding tanks), surrounding (moisture, dust)
↓	
Filtration	Equipment (ripeners, strainers, sieves, clarifiers, filters, heaters), containers, surrounding
↓	
Settling	Containers (buckets, ripeners, storage tanks), surrounding (moisture, dust, high temperature)
↓	
Bottling	Equipment (bottling and sealing machines), containers (jars, beers, bottles), dust, moisture, highg temperature

Příloha 1b: Abstrakt přihlášený na konferenci ESAS 2014.

DIRECT SAMPLE INTRODUCTION FOR ICP-OES HEAVY METAL DETERMINATION IN HONEY

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Cumulation of heavy metals in organisms can result in negative health effects. Nutrition is one of the possible ways for their intake. Honey is a natural dietary supplement containing health-beneficiary substances (vitamins, enzymes, etc.), but in case of its contamination can facilitate to introduce toxic metal into consumers' bodies. Being the final product of honey-making process, during which nectar or honeydew are gathered in wide surroundings of the beehive (relative to bee size) and can be used for monitoring of local environment's state of pollution [1,2]. Element mapping in various honey samples can be used for determination of its origin, too[3].

Preparation of honey liquid samples for AAS or ICP OES measurements usually involves either dry ashing in muffle furnace or nitric acid digestion. As all manipulations with material are sources of increased uncertainty, the direct analysis of honey samples using electrothermal vaporization for introducing sample into ICP OES was evaluated. The only manipulations were dilution of (1:5) honey samples to allow better liquid handling and addition of internal standard. Because the honey matrix composes mostly of monosaccharides (ca. 70%) on the contrary to plant material [4], effect of employing modifier gas was assessed. Method parameters were tested and compared to results obtained by liquid-sample introduction ICP OES analyses of respective honey digests and dilutes.

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Příloha 2: výpis z OBD - výsledky publikační činnosti podpořené projektem

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