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Determination of cadmium residues in bee products using a 'lab-made' bismuth bulk electrode

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ABSTRACT

Raw propolis and bee pollen has been widely used in different areas such as medicine, food and apitherapy because they have biological and medicinal properties. The beneficial effects of both bee products for human health include antibacterial, antiviral, antimicrobial and anti-inflammatory properties. However, hives exposure to heavy metals, due beekeeping practices and environment, is one of the problems facing beekeepers. The presence of cadmium in bee products should be controlled, because of its high toxicity. A lab-made Bismuth Bulk Electrode (BiBE) was developed for cadmium residue determination in Argentinean bee products such as raw propolis and bee pollen employing square wave anodic stripping voltammetry (SWASV) as electrochemical technique. The SWASV parameters were optimised based on a 2⁵ factorial design. The method presents a linear range from 2.00 to 100.0 µg L⁻¹ of Cd (II) with a limit of detection (LOD) and a limit of quantitation (LOQ) of 0.78 µg L⁻¹ and 2.61 µg L⁻¹, respectively. The repeatability was 8.03%, calculated as the relative standard deviation. Recovery experiments were performed using spiked raw propolis and bee pollen samples with standard deviation values from 1.16% to 7.20%. The BiBE is easy and fast to elaborate and the propose method is environmentally friendly and low cost. Then, it can be considered as a good alternative to the quality control of bee products due to its importance in the beekeeping industry.

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1. Introduction

Bees are flying insects known for their role in the pollination of agricultural crops and in producing natural products. The major bee product exploited worldwide is honey, not only for being a sweetener and natural preservative, but also for its biological properties used by alternative medicine [1]. Nowadays, the use of other bee products with medicinal properties and apitherapy is increasing. Within bee products, raw propolis and bee pollen have biological properties, such as antimicrobial and anti-oxidant effects, to be used in food and pharmaceutical industries [2,3]. Currently, the

consumption of nutraceuticals and functional food that provides nutrition and health benefits led to an increase in the exploitation of these products [4]. However, hives exposure to pollutants due beekeeping practices and from the environment is one of the problems facing beekeepers. Whereas bees fly over the area around their hive, they have contact with water, air, plants and soil, returning with contaminants and then brought into the hive. For this reason, their products have been used as biomarkers for monitoring pollutants, such as pesticides, heavy metals and others [5,6].

Nowadays, the existence of several health disorders generated by heavy metal intake and their accumulation in vital organs like kidney, liver and bones [7] is known. Cadmium is one of the toxic heavy metals which concentration in food stuff should be controlled, because of its high toxicity to extremely low levels [8]. Only a minimum amount of cadmium can be incorporated into the hive by air. However, soil contaminated by industrial and incinerator emissions allow cadmium reaches the nectar of plants. Bees gather the pollen and nectar of these plants and hence pollutants reached the hive and bee products [5].

In Argentina, there are few regulations about contaminants in bee products. Although the presence of cadmium is hazardous to human health, only lead and arsenic are controlled as metal contaminant in raw propolis and propolis extracts [9]. On the other hand, until now, there are no regulations for bee pollen quality control.

Cadmium determination is commonly performed by expensive techniques such as Atomic Absorption Spectrometry (AAS) [10], Mass Spectrometry with Inductively Coupled Plasma (ICP-MS) [11] or Atomic Fluorescence Spectrometry (AFS) [12]. Electrochemical techniques such as anodic stripping voltammetry with square wave detection can be used as an alternative due its low cost, fast and high sensitivity [13]. The use of bismuth – based electrodes is well known as an environmentally friendly material for replacing mercury film and drop electrodes for electrochemical stripping analysis. Their low toxicity, adaptability and low cost make them an excellent option since their presentation in 2000, and had their upswing in 2008 [14]. Bismuth has the advantages to have a wide potential window, forms alloys with heavy metals and have a high hydrogen over potential [15–17]. Many materials have been employed to generate bismuth films electrodes and coated bismuth electrodes, such as glassy carbon [18–20], pencil lead [21] and noble metals [22,23]. Nevertheless, bismuth bulk electrodes must also be consider as a successful alternative, due of the advantage of been economical, easy to fabricate, stable and have reproducible electrochemical signals [24]. So far, bismuth bulk electrodes were satisfactorily used for the determination of heavy metals on environmental samples, like sewage sludge and water samples (lakes, sea, rivers, tap and rain water) [25–27].

For the previously mentioned reasons, this work presents the application of a lab-made bismuth bulk electrode for the determination of cadmium residues concentration in complex samples such as raw propolis and bee pollen, using square wave anodic stripping voltammetry. In order to optimise the electrochemical parameters, a factorial 2^5 design was employed.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade and solutions were prepared using ultra-pure water (18 M Ω). Cadmium working solution was prepared by a proper dilution of the atomic absorption standard solution (1.000 g L⁻¹, Merck). Acetate buffer solution 0.1 M pH 4.5 was used as supporting electrolyte. All the experiments were carried out at room temperature and without removing oxygen.

2.2. Instrumentation

All voltammetry measurements were performed using an Epsilon potentiostat (BASi-Bioanalytical System, USA) and run with electrochemical analysis software. A standard three-electrode configuration was used consisting of a BiBE as the working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and a platinum wire as the counter electrode. These last two electrodes were provided from the BASi-Bioanalytical System.

2.3. Bismuth bulk electrode preparation

A Bismuth Bulk Electrode (BiBE) was design and implementation in the laboratory. For this proposed, solid bismuth was melted into a quartz capillary mould. After cooling, the capillary was broken resulting in a solid bismuth cylinder (2 mm diameter). At one end of the bismuth bar, a copper connector was welded with tin. Finally, this structure was cleaned with ethanol, to remove oiliness, and inserted inside a Teflon cylinder with 6 mm of external diameter. The exposed face of bismuth was polished with a waterproof sand paper until obtain a smooth surface of the metal. Then, an additional polishing was performed with alumina of 0.3 and 0.05 μm particle size and then thoroughly rinsed with ultra-pure water. A scheme and a picture of the BiBE are shown in Figure 1.

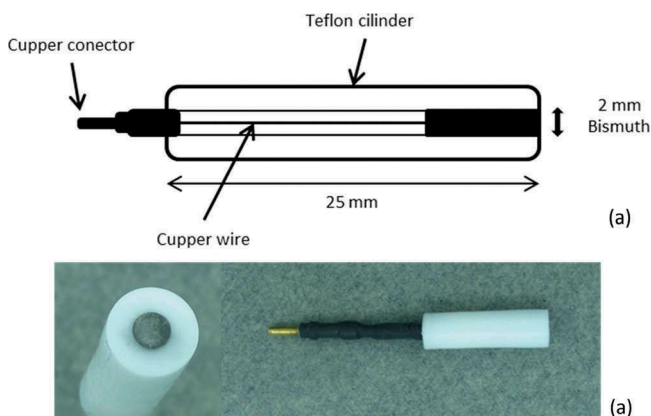


Figure 1. 'Lab-made' Bismuth Bulk Electrode scheme (a) and photograph of the electrode surface and body (b).

2.4. Procedure for square wave anodic stripping voltammetry measurements (SWASV)

The experiments were carried out in an electrochemical cell of 25.0 mL with the three electrodes immersed in sodium acetate buffer solution pH 4.5. In order to increase the bismuth conductivity, a thin layer of bismuth (III) oxide was obtained by cycling twice between -1.50 and 1.00 V [17]. The square wave anodic stripping voltammetry (SWASV) analyses were performed under optimised voltammetry conditions, with a deposition potential of -1.40 V for 180 s under stirring. After 10 s of quiet time, voltammograms were recorded in square wave voltammetry from -1.40 V to -0.40 V. In order to clean the electrode surface among each measurement, a cleaning step had taken place by applying 0.30 V during 30 s under stirring conditions. The square wave voltammetry parameters were selected as: step potential (ΔE_s) 6 mV, frequency (f) 20 Hz and amplitude of the square wave (ΔE_{SW}) 40 mV. To optimise electrochemical parameters, a factorial 2^5 design was used employing the maximum cadmium oxidation peak current as response.

2.5. Samples preparation

Raw propolis and bee pollen samples were obtained from several beekeepers at two different localities of Buenos Aires Province, Argentina: Bahía Blanca and Hilario Ascasubi. Samples treatments were carried out for further cadmium determination.

2.5.1. Raw propolis

An appropriate amount of raw propolis was weighted and calcined to white ashes in furnace at 400°C . Then, the white ashes were taken up with 20% (v/v) nitric acid solution, filtered and made up to 25.0 mL with water [9].

2.5.2. Bee pollen

For bee pollen pretreatment a wet digestion was employed [28]. For this purpose, a proper amount of dry pollen was weighted and digested with concentrated nitric acid under heating for 20 min. Then, the digested samples were filtered and made up to 25.0 mL with sodium acetate buffer.

3. Results and discussion

3.1. Optimisation of analytical parameters

A factorial 2^k response surface design (with k factors) is frequently used, in which a maximum and a minimum value are set for each parameter, establishing the experimental domain. In this work, a full factorial 2^5 experiment was employed to optimise SWASV parameters, which include all the possible combinations for the experimental factors levels selected and the study of interaction between the variables of interest [29]. The electrochemical parameters optimised are: step potential (ΔE_s), frequency (f), amplitude of the square wave (ΔE_{SW}), deposition potential (E_{dep}) and deposition time (t_{dep}). The net peak current is used as an analytical response. The levels for all variables were selected based on screening studies. Table 1 shows the two levels -1 and $+1$, the star points $-\alpha$ and $+\alpha$, and the value for each parameter investigated.

Table 1. Experimental values for each level studied.

Variable	- α	-1	0	+1	+ α
ΔE_s [mV]	2	3	4	5	6
f [Hz]	20	24	30	36	40
ΔE_{sw} [mV]	20	24	30	36	40
E_{dep} [V]	-1.40	-1.34	-1.25	-1.16	-1.10
t_{dep} [s]	30	60	105	150	180

The design was performed in thirty-five experiments, including thirty-two experiments for the cube and star points, and three for the central point experiments. All of them were conducted randomly and the experimental data obtained were analysed using ANOVA. The Pareto chart shown in Figure 2, indicates which factors and their interactions are important or significant. It can be observed that the main factors E_{dep} (A), f (B), ΔE_{sw} (D), t_{dep} (E) and their interactions were significant at a level 0.05. Furthermore, the interaction E_{dep} by ΔE_s (AC) resulted significant, indicating that ΔE_s (C) and E_{dep} were not independent factors. From the chart analysis, it can also be observed that the most significant effects were: t_{dep} (E) and E_{dep} (A). ΔE_{sw} and t_{dep} had a positive effect on the peak current response for cadmium. By contrast, an increment on E_{dep} caused a decrease on the analytical signal.

The fitted surface response obtained can be represented for the following equation:

$$\begin{aligned}
 I_{p,n} = & -6.91 \times 10^3 - 6.53 \times 10^{-4} E_{dep} + 6.02 \times 10^{-1} f - 3.25 \Delta E_s + 2.45 \times 10^{-1} \Delta E_{sw} \\
 & + 2.32 \times 10^{-2} \Delta E_s \Delta E_{sw} - 1.29 \times 10^{-1} t_{dep} + 5.17 \times 10^{-4} E_{dep} f - 2.04 \times 10^{-3} E_{dep} \Delta E_s \\
 & - 6.90 \times 10^{-5} E_{dep} t_{dep} - 6.79 \times 10^{-3} \Delta E_{sw}^2 + 1.34 \times 10^{-3} \Delta E_{sw} t_{dep} + 1.43 \times 10^{-4} t_{dep}^2
 \end{aligned}
 \quad (1)$$

with a (R^2) = 0.921, indicating a good fit. The corresponding surface responses obtained are shown in Figure 3. As can be seen, the optimum values are outside of the experimental region. Then, ΔE_s , f , ΔE_{sw} , E_{dep} and t_{dep} are set at the extremes of the surface response. Based on our previous screening analysis, lower and higher values of f and ΔE_s

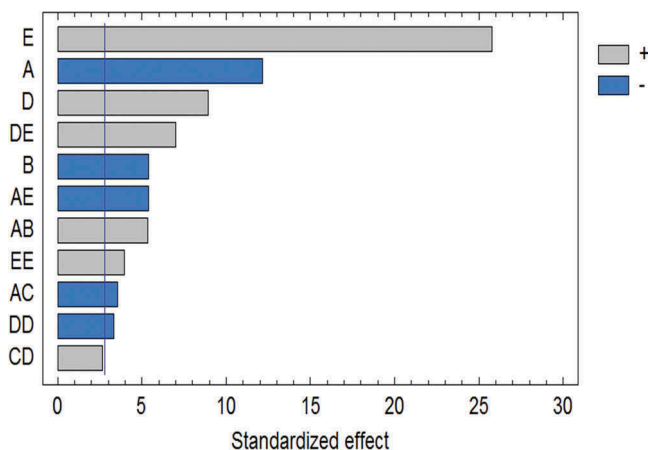


Figure 2. Standardised main effect Pareto chart for the 2 5 full factorial design. The significant level $p = 0.05$ is indicated by the vertical line.

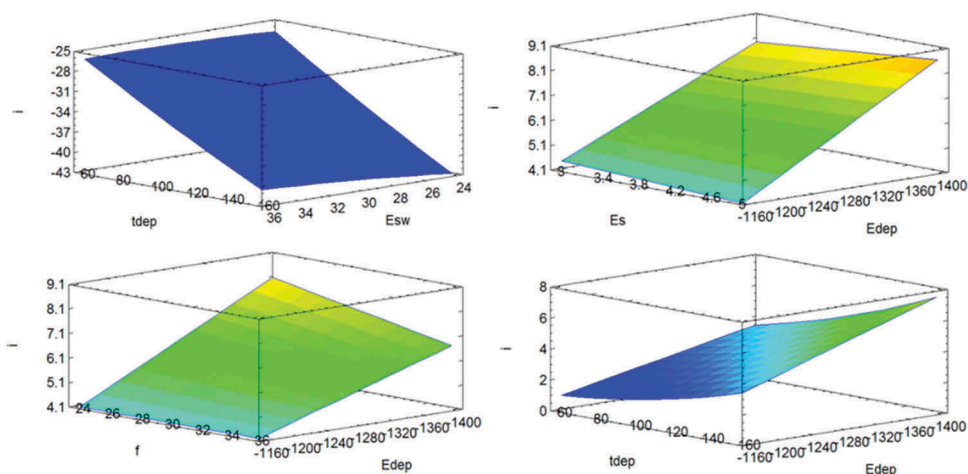


Figure 3. Response surfaces for the 2^5 factorial design.

respectively, were not significant. As well as, $\Delta E_{SW} = 40$ mV was selected as optimal for this work, taking into account that Liu et al. (2008) had studied that ΔE_{SW} values higher than 50 mV cause peak broadening [30]. E_{dep} more negative than -1.40 V generates hydrogen bubbles which decrease the selectivity of the electrode [31]. Also, higher deposition times than 180 s was not studied, because it would generate long time of analysis.

The optimum SWASV parameters were considered as $\Delta E_s = 6$ mV, $f = 20$ Hz, $\Delta E_{SW} = 40$ mV, $E_{dep} = -1.40$ V and $t_{dep} = 180$ s.

3.2. Analytical parameters

As can be seen in Figure 4, under the optimal experimental conditions, a linear concentration range was obtained from 2.00 to 100.0 $\mu\text{g/L}$ of Cd. The calibration curve was $I_{p,n} = (0.268 \pm 0.051) + (0.374 \pm 0.001) C_{Cd}^*$, where $I_{p,n}$ represents the net peak

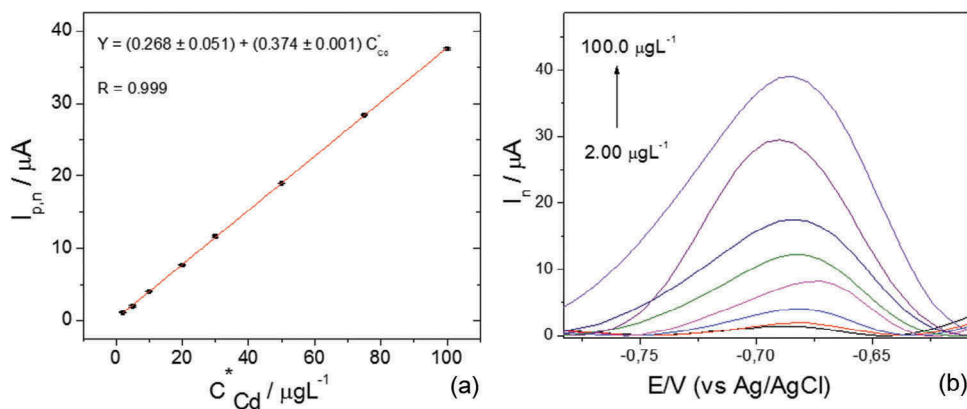


Figure 4. Calibration curve at optimal SWASV conditions.

Table 2. Comparison of the present manuscript with others electrochemical methods found in literature.

ELECTRODE	Method	Linear range [$\mu\text{g L}^{-1}$]	LOD [$\mu\text{g L}^{-1}$]	Reference
BDD (Boron-doped diamond electrode)	SWASV	19.80–243.9	1.0	33
P(DPA-co-2ABN)/GC-ME (Glassy carbon electrode modified with a film of Poly(diphenylamine-co-2-aminobenzonitrile)	DPASV	1.26×10^3 – 9.07×10^5	255	34
PANI/GCE (Glassy carbon electrode modified by conductive polyaniline coating)	SWASV	0–224.8	14.61	35
BDD (Boron-doped diamond thin-film)	DPASV	1–1000	1.0	36
Hg-GC (Hg-coated on a glassy carbon electrode)	DPASV	1–1000	1.0	
BBE (Bismuth bulk electrode)	SWASV	2.00–100.0	0.78	Proposed method

current and C_{Cd}^* the cadmium concentration ($\mu\text{g/L}$). The correlation linear coefficient (R^2) was 0.999. The limit of detection (LOD) and limit of quantitation (LOQ) were 0.78 and 2.61 $\mu\text{g/L}$ estimated as 3 and 10 times $S_{y/x}$ /slope respectively [32]. As can be seen in Table 2, LOD value is lower than others electrochemical methods found in the literature when cadmium is determined as single analyte [33] or in simultaneously of lead [34,35] and zinc [36]. The repeatability was 8.03% calculated as the percentage of variation relative standard deviation of eight independent measurements of a 30.0 $\mu\text{g/L}$ Cd solution.

3.3. Interference study

It is known that as raw propolis and bee pollen samples may contain other heavy metals such as lead and zinc. Nevertheless, under the working conditions, these metals do not interfere on the cadmium determination, because they have different oxidation potential values (Pb -0.5 V and Zn -1.1 V) [21,37]. Figure 5, shows SWASV voltammograms of a raw propolis a) and bee pollen b) samples with and without addition of cadmium. As can be seen, there is no interference in the potential ranges studied.

3.4. Application to propolis and pollen samples

The proposed electroanalytical method was applied to determine cadmium in raw propolis and bee pollen samples, using the optimum experimental conditions. Cadmium content in the samples analysed by inductively coupled atomic emission spectrometry technique (ICP-AES), was negligible. Therefore, taking into account the likely level of cadmium in samples of Buenos Aires province, Argentina, different aliquots of this analyte were added. All spiked samples were analysed in triplicate. The obtained results are shown in Table 3.

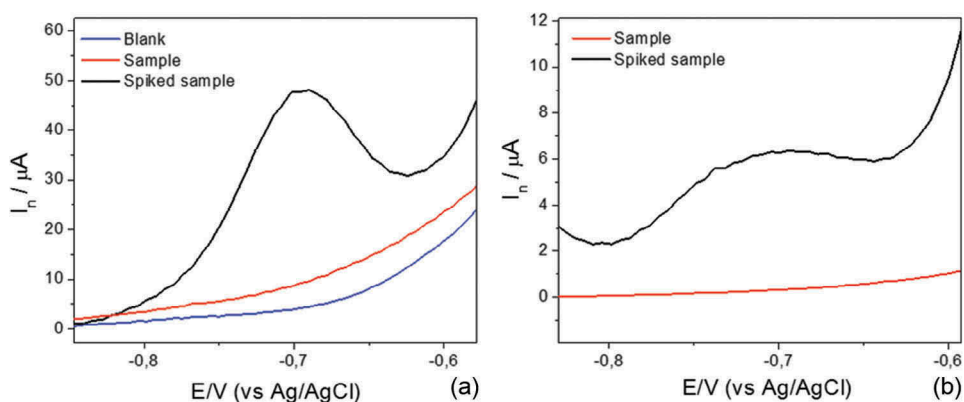


Figure 5. SWASV voltammograms of analysed samples in acetate buffer solution 0.1 M pH 4.5. (a) Raw propolis sample without and spiked with $30.0 \mu\text{g L}^{-1}$ Cd. (b) Bee pollen sample without and spiked with $6.0 \mu\text{g L}^{-1}$ Cd.

Table 3. Analysis of real samples.

Samples	Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery %	RSD %
Raw propolis ^a				
M1	30.0	31.9	106.3	4.01
M2	30.0	27.8	92.7	1.83
Bee pollen				
M1	6.00	6.07	101.1	3.21
	10.0	9.29	92.9	2.99

^a Samples were analysed by triplicate.

4. Conclusion

Cadmium residues determination in bee products, like Argentinean bee pollen and raw propolis, using square wave anodic stripping voltammetry (SWASV), was performed with a bismuth bulk electrode (BiBE). The proposed method is a good alternative for the environmental quality control of these products. A 2^5 factorial design was employed to optimise the SWASV parameters. The linear response was obtained in the range of 2.00 – $100.0 \mu\text{g L}^{-1}$ of Cd (II) with a limit of detection (LOD) of $0.78 \mu\text{g L}^{-1}$. The method also presented a good repeatability (8.03%) and recovery experiments were performed with a standard deviation values until 7.20%. Due to the advantages of being low cost, easy and fast to fabricate, BiBE could be consider as an alternative electrode to be used in voltammetry techniques for cadmium determination in bee products. Furthermore, bismuth is an environmentally friendly material with low toxicity, becoming a good substitute to the commonly used mercury electrodes.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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