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Integrating Molecularly Imprinted Polymer Beads in Graphite-Epoxy Electrodes for Voltammetric Biosensing of Histamine in Wines

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Abstract

This manuscript presents a voltammetric biosensing study with use of molecularly imprinted polymers to detect histamine in wine. Polymer beads were synthesized by standard precipitation polymerization method and implemented on the electrode surface via sol-gel immobilization. Scanning and confocal microscopy examinations permitted the characterisation of the material. Adsorptive stripping voltammetry in differential mode was the technique chosen for final application, selecting an enrichment time of 5 min. These conditions permitted a limit of detection of 0.19 μg·mL⁻¹ (1.0 μM), with a linear response range from 0.5 to 6.0 μg·mL⁻¹ (2.71 to 32.4 μM). The repeatability of the measurements was 4.6% relative standard deviation (n=12). Principal component analysis showed the ability of the prepared receptor for discriminating other biogenic amines and potential interfering species. A final application illustrating the determination of histamine was completed to show agreement of results.

Keywords:
Molecularly imprinted polymer; sensors; biogenic amines; histamine; voltammetry.
1. Introduction

Biogenic amines (BAs) can be found in different foods and beverages associated to their microbiological degradation; they involve several chemical species such as histamine, tyramine, cadaverine and putrescine, among others, normally originated from decarboxylation of aminoacids. BAs are considered a hazard from biological and chemical point as they are indicators of improper preservation of food. Moreover, they can be measured as control parameter indicating storage, monitoring and hygienic condition of several types of food and beverages. From physiological point of view, these chemical family can cause disorders and health problems that include several clinical profiles related with toxicological [1] issues like gastric and intestinal problems or allergic responses [2]; other type of common symptomatology like headaches, nausea and asthma [3] can also occur. Despite of the awareness that BAs may become toxic, it is difficult to establish a level of toxicity because of their chemical variety, their presence in different types of food and beverage stuff and the difficulty to associate the symptomatology to their ingestion. Among BAs, histamine is the most common one because of its abundant presence in fermentation and degradation processes, especially in fish, meat, egg, cheese, beer or wine because of the decarboxylation of free histidine by histidine decarboxylase enzyme [4]. It is reported that *Leuconostoc mesenteroides* bacteria have a high potential to produce histamine and tyramine in wine [5]. In the beverage field, it can be considered that the latter can be present at concentration levels of 5-50 mg·dm⁻³ [6]. Despite BAs have been examined by classical methods such as HPLC [7] and GC [8], nowadays they are also determined by immunoassays [9], sensors [10] and biosensors [11]. Classical chromatographic methods are expensive, time consuming, less efficient and qualified personnel is needed to perform pre-treatment, analysis and determination of BAs. For these reasons, (bio)sensors can be a good option to minimize cost and optimize the determination of BAs [12].

Molecularly imprinted polymers (MIPs) are artificial receptors based on host-guest principles with the aim of creating cavities in a polymeric matrix which are specific for a molecule or molecule moiety [13]. Moreover, they are highly crosslinked and contain recognition sites mimicking antibody function [14][15]. The synthetic nature of MIPs gives this material interesting properties such as versatility, robustness, cost effectiveness and the possibility to work out of physiological conditions in terms of pH, temperature and ionic strength among others [16]. Specially, performance of these new
materials is to be emphasized because of their non-denaturing and reusable features. Notwithstanding these noticeable benefits, there are important difficulties in integrating this material on sensors and biosensors, a challenging field that attracts the interest of the scientific community worldwide [17][18].

Several alternatives have been described employing biosensors using MIPs for BAs detection, e.g. the use of a quartz crystal microbalance [19], the use of a colorimetric sensor array [10], fluorescence detection using graphene and quantum dots [20], electrochemical MIP beads integrated in a carbon paste electrode [21], solid-phase imprinted nanoparticles as recognition elements in polymeric matrix ion selective electrodes [22] or sol-gel SiO$_2$ layer presenting absorbance sensing for BAs [23].

It is needed to highlight two interesting works that appeared in recent literature. One employs a magnetic-bead functionalized with MIPs which uses magnetic-MIPs to preconcentrate the samples, improving the yield in the washing steps and minimizing the matrix effect [24]; the other one features an assay equivalent to an immunoassay with specific MIP and fluorescence detection in a fish matrix [25]. Specific MIPs for BAs have been also employed to perform solid phase extraction from wine matrix [26].

The main objective of this report is to develop an electrochemical sensor based on the use of MIPs as recognition elements for histamine detection, with use of the differential pulse voltammetry technique and with application on wine matrix. In the present trend of increasing selectivity and sensitivity of analytical procedures, molecular imprinting technique is one of the most effective, cheap and simple methods used in molecular recognition. In this context, MIP bead particles were synthesized and integrated onto graphite epoxy composite (GEC) electrodes using a sol-gel immobilization matrix. Then, their responses towards histamine were investigated and compared to those of non-imprinted polymer and bare GEC electrodes. This characterization is completed with a study of the specificity of this MIP sensor with another BAs and analogue compounds that also can be found in wine matrix. Final determination in wine matrix and comparison against the reference method concluded the work done.

2. Materials and methods

2.1. Chemicals and reagents
Reagents used were analytical reagent grade and all solutions were made up using MilliQ water from MilliQ System (Millipore, Billerica, MA, USA). Tetramethyl orthosilicate (TEOS), hydrochloric acid, sodium hydroxide, gallic acid, p-coumaric acid, and o-phthaldialdehyde (OPA) were purchased from Sigma-Aldrich (St. Louis, Mo, USA). Ethylene dimethacrylate (EGDMA) was purchased from Fisher Scientific. Methacrylic acid (MAA), phosphoric acid, histamine dihydrochloride and tyramine hydrochloride were purchased from Acros Organics (Belgium). Methanol (MeOH), Ethanol (EtOH) and Acetic acid (HAc) were purchased from Scharlab (Barcelona, Spain) and 2,2'-azobis(2,4-dimethylvaleronitrile) (AIVN) was purchased from Wako Chemicals GmbH (Neuss, Germany). Graphite powder (particle size < 50 μm) was received from BDH (BDH Laboratory Supplies, Poole, UK) and Resineco Epoxy Kit resin was supplied from Resineco green composites (Barcelona, Spain). The final experiment samples were prepared in phosphate buffer (100 mM KCl, 42 mM K₂HPO₄·2H₂O, 8 mM KH₂PO₄, pH 7.0).

2.2. Instrumentation

All polymerisations were done in a water bath controlled with a Huber CC1 thermoregulation pump (Huber GmbH, Offenburg, Germany). The electrochemical measurements were performed with PalmSensTM potentiostat with a four-channel working electrodes (Palm Instruments BV, Houten, The Netherlands) and using a commercial 52–61 platinum combined Ag/AgCl reference and counter electrode (Crison Instruments, Barcelona Spain). Fluorimetric measurements were recorded on a Fluorolog 1 Modular spectrofluorometer (Horiba Jobin Yvon, France). All the synthesized polymers were characterized by scanning electron microscopy (SEM) by using a scanning electron microscope EVO®MA10 operated at 30 kV. The sensors were examined with MERLIN-FE-SEM microscopy operated at 15 kV. Confocal Microscopy inspections were performed with a TCP-SP5 Leica microscope.

2.3. Software and data processing

The electrochemical measurements were done with Multitrace 4.2. software (Palm Instruments BV, Houten, The Netherlands). The resulting microscopy images were treated with Fiji package software and Image J software (Zeiss GmbH, Jena, Germany) and Origin 8.0. Principal Component Analysis (PCA) were programmed by the authors.
using MATLAB 2016b (MathWorks, Natick, MA); while the graphical representation and analysis of the results was performed with Sigmaplot (Systat Software Inc., San Jose, CA).

2.4. Polymer synthesis

0.5 mmol of histamine dihydrochloride was weighted and transferred to into a 250 mL round bottomed flask and dissolved with 40 mL of ethanol. Subsequently, 2.05 mmol of MAA were added into the flask and the mixture was stirred gently for 15 min. An amount of 10.2 mmol of EGDMA and 0.10 mmol of AIVN were then added and the mixture was purged with a flow of dry nitrogen for 10 min. Polymerization was initiated in a water bath at 60°C for 17 h with magnetic stirring. After MIP was dried for an overnight at room temperature, it was extracted with methanol:acetic acid (9:1, v/v) using a Soxhlet system for 72 h. Non-imprinted polymers (NIPs) for comparison purpose were synthesized in the same manner described above, but without the addition of the template histamine.

2.5. MIPs integration onto sensor via sol-gel immobilization

Biosensors were prepared by sol-gel immobilization of the polymer beads on the carbon electrodes; this consists essentially on creating an appropriate conductive gel which incorporates the insulating polymer micro beads. When it is prepared it can be deposited onto the sensor surface of a graphite epoxy composite (GEC) [27] for sensing purposes. For the sol-gel preparation 0.5 ml of TEOS, 0.5 mL of EtOH, 0.25 mL of H₂O and 25 µL of HCl 0.1 M were vigorously mixed for 45 min and then rested 35 min in order to achieve the optimal polymerization conditions. Then 0.2 mL of the rested solution were added to a 7 mg of graphite and 40 µL of a 15 mg·mL⁻¹ polymer (HISTAMINE-MIP) suspension in EtOH. 40 µL of EtOH were added to obtain a sol-gel modified electrode which was used as a control. This mixture was stirred for 10 min at 1400 rpm. The surface then spin-coated was by depositing 10 µL of the solution onto the surface and spin using a home-made spin-coater. Equivalent control sensor was prepared using 40 µL of a 15 mg·mL⁻¹ NIP beads suspension for comparison purpose. Preparation of the biosensors was finished drying the electrodes overnight at 4°C [28].
2.6. Electrochemical measurements

A first enrichment step was performed without polarization of the sensor. Next, stripping was achieved with the differential pulse voltammetric technique. For this purpose, potential was scanned between 0 to 1.5 V at a scan rate of 100 mV/s, with a step potential of 5 mV and a pulse amplitude of 50 mV, without stirring. Different buffer solutions made of acetate (0.1 M CH$_3$COOH-CH$_3$COONa, pH 4.5), phosphate (0.05 M KH$_2$PO$_4$·K$_2$HPO$_4$, pH 6.0-7.0), and tris-hydroxymethyl-aminomethane buffer solution (0.1 M tris-HCl, pH 8.0-9.0) were prepared for pH optimization of the electrochemical measurements. All these solutions incorporated an additional 0.1 M KCl saline background for better electrochemical response. Final analytical curves were obtained by the addition of aliquots of the histamine standard solutions (1000 µg·mL$^{-1}$) into the measurement cell containing 20.0 mL of the pH 7.0 phosphate buffer solution. All electrodes were regenerated after each measurement by electrochemical cleaning, applying 1.5 V for 45 s in phosphate buffer pH 7.0 (the working solution). The cleaning is a key step to regenerate the polymers capacity of response, avoiding the unspecific interaction responses that may affect their capacity binding.

2.7. Real sample analysis

White wine samples were analysed in parallel with the developed sensor and with the OPA fluorimetric reference method, for comparison purposes. Histamine generates a highly fluorescent complex with o-phtaldialdehyde (OPA) that permits its determination at the ng·mL$^{-1}$ level. The complex absorbs at a wavelength of 350 nm and emits at 444 nm. It is important to mention that the reaction is stopped by phosphoric acid after 4 minutes of putting them in contact, being the complex stable for 2 hours; afterwards it is degraded and the fluorescence decays. To minimize sample matrix effects a previous extraction procedure is done. A wine aliquot of 25 mL was taken and its pH adjusted at pH=11 using NaOH 1M. Afterwards, this alkaline solution was transferred to an extraction funnel and 10 mL of n-butanol were added; then the solution was shaken during 5 minutes. The aqueous phase was removed from the funnel and 10 mL of HCl 0.1M were added; the funnel was then vigorously shaken during 5 min. The organic phase was removed and the fluorimetric reaction was produced in the aqueous phase by addition of the OPA reagent, where the histamine remains [29]. A calibration with
aqueous standards was performed without need of the extraction in order to obtain concentrations in the wine samples [30].

3. Results and discussions

3.1. Microscopy characterization

Once the synthesis was done for MIPs and NIPs, the size of the particles was compared using SEM microscopy before being immobilized into the sensor surface. Aluminium stubs were used as supports. A conductive carbon-tape or a conductive aluminium-tape was added to the aluminium surface. A small amount of sample of MIPs and NIPs was sprinkled into this. Then the conductive carbon-tapes were metalized by an Au-Pd alloy (80:20) during 4 min adding a 15-20 nm layer on the sample, which permitted to visualize the synthesized polymer beads with a good contrast. These polymer beads showed a non-regular spherical shape (see Figure SP1, supplementary material). The average size and standard deviation of MIPs and NIPs was, respectively, 0.61 ± 0.18 µm and 0.74 ± 0.19 µm (see Figure SP2, supplementary material). As can be observed there, both types of polymer particles presented a similar size and visual aspect which make the NIPs suitable to act as a control.

On the hand, Fig. 1 displays SEM images of the three types of biosensors used in this work once manufactured, MIP-modified, NIP-modified and graphite-epoxy composite as electrode controls. MIPs and NIPs were immobilized via sol-gel immobilization onto the GEC surface while GEC showed totally different surface. Apparently, there is a clear alteration in the surface roughness after the deposition of sol-gel while there are no clear differences between MIPs and NIPs; any difference of response is to be due by the imprinted sites towards histamine.

< Figure 1>

Confocal microscopy gave us a unique opportunity to characterize the differences between MIPs and NIPs complexing ability, if the fluorimetric OPA-histamine complex was created in situ. For this purpose, MIP and NIP beads were equilibrated with histamine at the same concentration of 5 µg·mL⁻¹ (in 0.1M HCl media) and a negative
control was also performed without placing histamine, that is, in absence of the complex. Next the reagent generating the fluorescent complex was added, as the developer of the interaction. As it is shown in Fig. 2, from left to, MIPs (A), NIPs (B) and negative control (C) presented different fluorescence caused by the developed OPA-histamine complex. In Fig. 2A MIPs exhibit a much higher intensity than NIPs (Fig. 2B), a proof of the specific capture through the imprinted sites generated. It is interesting to remark that the negative control (Fig. 2C) exhibits some degree of autofluorescence. A direct calculation permitted to establish that the MIP beads presented 5.4 times more fluorescence intensity than the NIPs, once deducted the background value.

< Figure 2 >

3.2. Electrochemical measurements

3.2.1. Influence and optimization of pH

Histamine is a strong base with two basic centres of pKa 9.4 for the side chain nitrogen, and pKa 5.8 for the imidazole nitrogens. Although the compound contains three nitrogens, it is a di-acidic base because of resonance in the imidazole nucleus.

Electroanalytical performance of the modified electrodes in the oxidation of histamine solution (5 µg·mL⁻¹) were investigated in various supporting electrolytes at different pH values by carrying out differential pulse voltammetric measurements. 0.1 M acetate buffer at pH 4.5, 0.05 M phosphate buffer at pH 6.0 and 7.0, and 0.1 M Tris-HCl buffer solutions at pH 8.0 and 9.0 were tested for this purpose. The pH of the supporting electrolyte has a significant influence on the electrooxidation of histamine at the modified electrode (see Figure SP3, supplementary material). For example, in acidic media, the NH₂− group of the analyte will protonate to NH₃+ and consequently the adsorptive mechanisms will change, resulting in a decreasing current for the histamine peaks in acidic solution (pH 4.5). Since the maximum peak current for histamine was recorded at pH 7.0, further experiments were performed at phosphate solution buffered at this pH. Furthermore, while histamine exists as positively charged at pH 7, the microparticles are negatively charged due to the deprotonated MAA (pKa = 6–7) moieties and thus, electrostatic interactions can also occur, providing proper conditions for enrichment in the adsorptive procedure explained next. The final utilizable signal was a single oxidation peak, centred at +1.10−+1.15 V vs. Ag/AgCl.
3.2.2. Contact time optimization

Contact time was another important parameter that was examined and optimized for the adsorptive stripping procedure. For this aim, the prepared electrodes were inserted into 5 µg·mL⁻¹ histamine solutions for various times, without any explicit polarization, and next, voltammetric determination was performed, observing oxidation of adsorbed analyte (see Figure SP4, supplementary material). According to this figure, increasing contact time leads to a marked increase in the observed peak current of histamine until about 5 min, when a turning point is perceptible. From this experience, an enrichment time of 5 min was chosen for further DPV experiments. The same behaviour was observed when this experiment was repeated at the 1 µg·mL⁻¹ histamine concentration. Obviously, the response characteristics can be modulated, if needed, by increasing the enrichment time if a lower concentration range is to be attained (or the contrary for a larger one).

3.2.3. Repeatability and reproducibility

The intra-day repeatability of the peak current magnitude was determined by successive measurements (n = 12) of a 5 µg·mL⁻¹ histamine standard in pH 7.0 phosphate buffer under the optimized experimental conditions. The relative standard deviation (RSD) was calculated as 4.62% (Fig. 3), indicating the good repeatability of the reported MIP sensor. These satisfactory obtained results demonstrate the correct choice in performing the electrochemical cleaning procedure between samples, that minimized cross-talk in analysis.

In order to evaluate the day-to-day reproducibility of the imprinted sensor, three different calibration curves were carried out in three different days, as detailed in Table 1. Reproducibility of these measurements was calculated as 2.61% RSD, extracted from the variation of the slopes. These results showed that the sensor had a remarkable reproducibility, again thanks to the proper definition of the measuring protocol.
3.2.4. *Calibration study*

The calibration plot was constructed from the DPV response, illustrated in Fig. 4; this clearly shows two linear segments, probably caused by the saturation of the amount of available recognition sites in the MIP beads. The MIP sensor presented thus a good linear relationship in the lower range, starting from 0.5 µg·mL\(^{-1}\) to 6.0 µg·mL\(^{-1}\) (or 2.7–32.4 µM). The linear regression equation was determined as follows: \(Y = 4.9416C - 0.0779\) \((R^2 = 0.9992)\). The limit of detection (LOD) and limit of quantification (LOQ) were calculated as 3S/m and 10S/m respectively, where S represents the standard deviation of the regression and m is the sensitivity of the calibration. The LOD and LOQ values were calculated as 0.19 µg·mL\(^{-1}\) (1.0 µM) and 0.62 µg·mL\(^{-1}\) (3.4 µM), respectively.

<Figure 4>

3.2.5. *Interferents*

In order to evaluate the response of the MIP sensor in wine matrix different compounds were evaluated. In addition to histamine the compounds chosen were tyramine, as a second, related compound, biogenic amine and coumaric acid and gallic acid, as potential polyphenolic interfering species in the wine matrix.

The tool employed to analyse the different voltammetric response was principal component analysis (PCA). Calibration curves were performed for tyramine, coumaric acid and gallic acid and its voltammetric responses were analysed using PCA. As can be seen in Fig. 5 histamine forms a very distinct cluster indicating a differentiated voltammetric response, and only coumaric acid and tyramine are confounded by the prepared sensor, an insignificant fact, as their detection is not the desired purpose.

<Figure 5>
3.3. Application to real sample analysis

In order to evaluate the feasibility of the proposed imprinted sensor wine samples were analysed by electrochemical method and compared with the fluorimetric reference procedure, in accordance with standard international recommendation [30]. Previously, the histamine peak could not be seen in beer samples at +1.10 V, suggesting an extremely low level which forced us to consider only wines. The electrochemical method was performed with histamine ranging from 2 to 12 µg·mL⁻¹ in phosphate buffer at pH 7. The comparison results of the two methods are summarised in Table 2. It can be observed that the electrochemical results obtained from wine samples were similar to the gold standard fluorimetric method. The standard deviation for fluorimetric procedure was slightly better than the electrochemical one, probably due to the matrix effect of the wine samples in the electrochemical method, while the fluorimetric one was performed by direct extrapolation from a linear regression to obtain the concentration values. Also, it used one extra replicate, that probably could also improve this feature.

4. Conclusions

This manuscript reports a biosensor based on molecularly imprinted polymers used as recognition elements for histamine detection and integrated in voltammetric sensors. MIPs and NIPs were successfully synthesized and presented a similar, highly porosity morphology that made them comparable. Confocal microscopy showed an increasing binding capacity for OPA-histamine complex in the MIPs when compared with the control. The integration of the polymers onto GECs surface via sol-gel immobilization provided a homogeneous layer that allowed a satisfactory preconcentration of histamine in wine. The biosensor presented a linear range from 0.5 µg·mL⁻¹ to 6.0 µg·mL⁻¹ and a LOD of 0.19 µg·mL⁻¹ for histamine, values that could be diminished for longer enrichment times. The study of interferents demonstrated a good capability for histamine discrimination as the voltammetric signals from the interferents was clearly distinct from the histamine signal. The method disclosed herein is compared with the reference fluorimetric method for histamine detection in white wine samples; the results obtained with the presented electrochemical method show comparable performance with the reference method. The alternative presented, that combines molecular imprinting technology and electrochemical sensing, provides a fast, robust, on-site and
cost-effective method that is comparable with official methods. Finally, it has to be remarked the effectiveness and simplicity of the concepts applied in this work, which in addition can represent a generic universal approach that may be custom-adapted to any given analyte with the only condition that allows for the imprinting.

**Acknowledgments**

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**References**


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Table 1. Day-to-day reproducibility of calibration of a given histamine MIP biosensor

<table>
<thead>
<tr>
<th></th>
<th>Slope (µA mg^{-1}·L)</th>
<th>Intercept (mg·L^{-1})</th>
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<td>0.9989</td>
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<tr>
<td>Day 2</td>
<td>4.675</td>
<td>0.184</td>
<td>0.9997</td>
</tr>
<tr>
<td>Day 3</td>
<td>4.816</td>
<td>0.166</td>
<td>0.9989</td>
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</table>
**Table 2.** Results obtained for two wine samples using the developed MIP biosensor, in comparison with the reference fluorimetric method.

<table>
<thead>
<tr>
<th>Replicate</th>
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<th>VOLTAMMETRIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wine1 (mg·L⁻¹)</td>
<td>Wine2 (mg·L⁻¹)</td>
</tr>
<tr>
<td>Replicate1</td>
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</tr>
<tr>
<td>Replicate2</td>
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<td>Replicate4</td>
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<tr>
<td>s (ppm)</td>
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<td>0.012</td>
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</table>
FIGURE CAPTIONS

**Figure 1.** SEM images of the MIP beads (A) and NIP beads (B) immobilized via sol-gel and bare graphite-epoxy composite (GEC) electrode (C).

**Figure 2.** Confocal microscopy of MIP beads (A) and NIP beads (B) after contact with a 5 µg·mL⁻¹ histamine-OPA complex. (C) background fluorescence of MIPs as a negative control. (D) Fluorescence Intensity (a.u.).

**Figure 3.** Repeatability measurements (n=12) of biosensors prepared from MIP beads, NIP beads and comparison against the bare graphite-epoxy composite (GEC) electrode.

**Figure 4.** Adsorptive DPV response of the developed sensors against histamine (phosphate buffer pH=7.0).(A) Generic calibration range examined with the inset of the low concentration linear range; (B) Obtained voltammograms for the MIP sensors; (C) Obtained voltammograms for the NIP sensors.

**Figure 5.** Multivariate transformation using principal component analysis (PCA) of the voltammetric responses of the selectivity features of the MIP-modified sensors; discrimination of histamine, gallic acid, p-coumaric acid and tyramine.
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5