A Highly Sensitive Impedimetric Metamitron Microsensor Based on All-Solid-State Membrane Using a New Ion-Pair Complex, [3,3'-Co(1,2-closo-C₂B₉H₁₁)₂][C₁₀H₁₁ON₄]+ †

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Abstract: An all-solid-state impedimetric microsensor based on impedimetric measurements for detecting the herbicide metamitron (MM) is reported in the present work. For this purpose, a novel metamitron ionophore has been prepared. It was based on the isolation of the metamitron monoprotonated form coupled to the metallocarborane anion, cobalt bis (dicarbollide), ([3,3'-Co(1,2-closo-C₂B₉H₁₁)₂]⁻) as an ion-pair complex of the type [3,3'-Co(1,2-closo-C₂B₉H₁₁)₂][C₁₀H₁₁ON₄]⁺. Once the ion-pair complex was synthesized, it was incorporated to a PVC-type membrane including o-Nitrophenyloctylether (o-NPOE) as plasticizer. The membrane was then drop-cast on top of polypyrrole-modified gold working microelectrodes. A quick response of 30 s has been provided by the microsensor in the range of metamitron concentrations between 10⁻⁸ M and 10⁻⁴ M with a limit of detection of 10⁻⁸ M. Furthermore, it was highly selective toward metamitron, when compared to some possible interfering compounds as imazapic and carbetamide.

Keywords: metamitron; ion-pair complex; microsensor; metallocarboranes; herbicides; triazines

1. Introduction

Herbicides are important components to control germinating weeds of which several categories are available on the market depending on several criteria such as the nature of weeding and the treated surface. Triazinic herbicides interfere in the photosynthesis of the plant and cause its death by starvation. This is why it is necessary to apply treatments with triazinic herbicides in areas where beets are grown. However, those compounds can affect sex differentiation by inducing an enzyme aromatase that converts androgens into estrogens, that acts on the functioning of animal’s hormonal system [1]. Some studies also showed that ovarian cancer risk in female farm workers increased due to long-term exposure to triazinic herbicides [2]. Metamitron (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5-one) is an asymmetric triazine herbicide used in pre-treatment of sugar beet, red and fodder beet crops and some varieties of strawberries to control broadleaf plants by interfering with their
photosynthetic cycle. Its maximum allowed concentration is 0.4 ppm in soil, 0.3 ppm in water and 0.5 ppb in working area air.

Mostly, metamitron is quantified using conventional chromatographic techniques such as HPLC and GC-MS among others [3]. However, this sophisticated instrumentation is expensive, time consuming and requires sample preparation.

In this context, electrochemical microsensors are presented as a very good alternative because of their small size, low-cost equipment and also faster analysis. The present work reports on a novel ion-pair complex \([C_{10}H_{11}O\text{N}_{4}]^{+}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]\) as the active component of a PVC-type polymeric sensitive membrane for metamitron detection. Metallocarborane anions of the type \([3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) have been reported for analysis applications due to their very good stability, when isolated with organic bases of the type \([\text{cation-NH}]^{n+}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) [4]. This strategy allows incorporating the target molecule to the sensitive membrane in order to improve the microsensor’s performance and selectivity. The metamitron-selective microelectrode was characterized using electrochemical impedance spectroscopy (EIS) following the generalized standard addition methods (GSAM) [5]. As a result, a very low limit of detection of \(10^{-8}\) M was found, which is 100 times lower than the maximal allowable concentration of metamitron in soils and water. The selectivity study also showed that the microsensor is highly selective toward metamitron even in the presence of imazapic and carbetamide which are usually present in the same media.

2. Materials and Methods

2.1. Preparation of the Ion-Pair Complex \([C_{10}H_{11}O\text{N}_{4}]^{+}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]\)−

The ion-pair complex \([C_{10}H_{11}O\text{N}_{4}]^{+}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) has been obtained by ion-exchange procedure. First, the \(\text{H}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) metallocarborane form was obtained by extracting an acidic solution of \(\text{Cs}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) in \(\text{HCl} 1\) M with diethyl ether. The organic layer was shaken three times with \(\text{HCl} 0.1\) M. Then, the solid residue was obtained after diethyl ether evaporation under vacuum. Subsequently, the solid obtained was diluted in deionized water to generate \(0.008\) M solution of \(\text{H}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) in \(\text{HCl} 1\) M with diethyl ether. The organic layer was shaken three times with \(\text{HCl} 0.1\) M. Then, the solid residue was obtained after diethyl ether evaporation under vacuum. Subsequently, the solid obtained was diluted in deionized water to generate \(0.008\) M solution of \(\text{H}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) (solution 1). Afterwards, metamitron was dissolved in deionized water to obtain \(0.008\) M solution (solution 2). Next, both solutions were mixed and, after stirring, a yellow precipitate was obtained. This was filtered off, then washed with \(\text{HCl} 0.1\) M and finally dried under vacuum.

2.2. Surface Modification

The device used in this work integrates an array of four gold working microelectrodes, two \(\text{Ag/AgCl}\) reference microelectrodes and one gold auxiliary microelectrode (Figure 1). The configuration of the transducer allows performing measurements of four microelectrodes simultaneously. This is very useful not only for future multi-detection applications where different herbicides can be detected simultaneously but also to obtain fast statistical values. The microelectrodes have been cleaned with ethanol, acetone and water. Then a polypyrrole (PPy) conductive layer has been electropolymerized onto the surface in order to increase the adherence between the membrane and gold.

The polymeric membrane selective to metamitron was made of \(31\%\) \(w/w\) of \(\text{PVC}\) as the polymeric matrix, \(65\%\) \(w/w\) of \((\alpha\text{-NPOE})\) as plasticizer and \(4\%\) \(w/w\) of \([C_{10}H_{11}O\text{N}_{4}]^{+}[3,3^{′}-\text{Co}(1,2\text{-closo-C}_2\text{B}_9\text{H}_{11})_2]^{-}\) synthetized ion-pair complex as the active site for metamitron recognition. All components were dissolved in \(1.5\) mL of \(\text{THF}\). Afterwards, \(2\) \(\mu\)L of the obtained liquid mixture were drop-cast onto the PPy modified gold working microelectrodes and let overnight for solvent evaporation.
3. Results and Discussion

The microsensor’s characteristic response was evaluated using the electrochemical impedance spectroscopy (EIS). For this purpose, standard solutions of metamitron from $10^{-8}$ to $10^{-4}$ M were prepared in a background of the redox couple $K_3[Fe(CN)_{6}]/K_4[Fe(CN)_{6}]$ 5 mM in phosphate buffer solution to maintain a pH of 7.2. All the measurements have been carried out in a potentiostat “BioLogic VMP3”, and an electrochemical cell based on four working microelectrodes, one saturated calomel reference electrode and one platinum counter electrode. Figure 2 shows the Nyquist diagrams corresponding to the different concentrations of metamitron. As it can be observed, the electrochemical impedance increases with the concentration of metamitron. Moreover, the metamitron-selective microsensor presents a limit of detection of 10 nM that covers the minimum allowable concentration value in the linear range from $10^{-8}$ M to $10^{-4}$ M. The time needed by the microsensor to achieve a stable response was found to be approximately around 30 s.

A cross-selectivity study was carried out to evaluate the influence of potential interferences to the microsensor’s response. The microsensor calibration was carried out using metamitron standard solutions to obtain a total concentration range from $10^{-8}$ to $10^{-4}$ M in 7 mL of 0.1 mM solution of imazapic or carbetamide respectively in the background of the redox couple $K_3[Fe(CN)_{6}]/K_4[Fe(CN)_{6}]$ 5 mM in phosphate buffer solution to maintain a pH of 7.2 used previously following the fixed interference method [6]. The obtained results are summarized in Figure 3.
The obtained results confirm the high selectivity of the microsensor towards metamitron in the presence of these structurally similar compounds. The small differences between the slopes ratify the fact that a high concentration of potential interferences around 0.1 mM which is almost the highest concentration that can be prepared in water according to their solubility values, presents negligible influence on the microsensor response confirming thus, the importance of incorporating the target molecule to the membrane in the form of ion-pair complex in order to improve the microsensor’s selectivity.

4. Conclusions

The conception steps and features of an all-solid-state and miniaturized metamitron-selective microsensor have been described. The ion pair complex $[\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_4]^+ [3,3'-\text{Co}(1,2\text{-closo-}\text{C}_2\text{B}_{9}\text{H}_{11})_2]^-$ has been synthesized and was included into a PVC-type polymeric membrane as the active site for metamitron recognition. The micro microsensor showed a limit of detection of 10 nM, a time of response estimated to be around 30 s and linear range of concentrations between $1\cdot10^{-8}$ M and $1\cdot10^{-4}$ M. The cross-selectivity study in the presence of imazapic and carbetamide showed that the microsensor’s response toward metamitron is highly selective. Furthermore, the miniaturized device developed is able to produce reliable and real-time data using four independent metamitron-selective microsensors simultaneously.

Author Contributions: Authors made substantial contributions to conception, design, and/or acquisition of data, and/or analysis and interpretation of data. Authors have also participated in drafting the article or revising it critically for important intellectual content and have given final approval of the version to be submitted and any revised version.

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References


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