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A COMPARISON OF DIFFERENT METHODS TO REMOVE DISSOLVED OXYGEN: APPLICATION TO THE ELECTROCHEMICAL DETERMINATION OF IMIDACLOPRID

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This study compares different methods for the removal of oxygen from the solution prior to the chronopotentiometric determination of the insecticide imidacloprid on glassy carbon electrode. The research included the application of the chemical method involving addition of sulfite ion, and the physical method of purging the sample with nitrogen stream, as well as their combination. By comparing analytical signals of imidacloprid, chemical method showed almost the same efficiency as conventional physical method, while the best reproducibility was achieved by applying chemical method with addition of the saturated sodium sulfite solution. The method is very simple and can be applied for deoxygenation of the solution prior to the chronopotentiometric analysis. The application of the chemical deoxygenation significantly shortened duration of the chronopotentiometric analysis of imidacloprid from approximately 15 min to 1 min.

KEY WORDS: imidacloprid, sulfite ion, chemical deoxygenation.

INTRODUCTION

Imidacloprid is a systemic insecticide that belongs to a group of neonicotinoids (1). According to the mechanism of action, it acts on the insect's central nervous system, causing irreversible blocking of postsynaptic nicotinergic acetylcholine receptors (1). Since its discovery and utilization in practical use, imidacloprid has become the most selling insecticide worldwide used for crop protection and pest control (1-3). Extensive usage of imidacloprid in agriculture requires a systematic control of its content in environmental samples.

Most of the methods used for the determination of imidacloprid are based on the use of chromatographic methods (4-7). Although these techniques exhibit high sensitivity and selectivity, they are complicated, time consuming, expensive, and require highly trained personnel. On the contrary, electroanalytical techniques are of great interest due to their advantages, including high sensitivity, comparative simplicity, rapid response and low

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cost. There are several studies about the application of electroanalytical methods for the determination of imidacloprid, which are based on the irreversible reduction of the analyte on the working electrode (8 - 10). This electroreduction is carried out in two steps. In the first step the nitro group is reduced to a hydroxylamine, and in the second step to an amine (8). Although the applied electrochemical techniques are of short duration and do not require complicated sample preparation, most of time before the analysis is spent on the removal of dissolved oxygen from the solution, as an inevitably required step in the imidacloprid electroanalysis.

The electrochemical reduction of dissolved oxygen results in high residual currents and the production of H_2O_2 and OH^-, which may affect the studied electrochemical process in a certain potential range (11, 12). Since imidacloprid is electroactive in the same potential range where oxygen reduction occurs, in order to avoid drawback procedures by dissolved oxygen, it has to be removed from the solution before the analysis. Therefore, many different methods are developed for deoxygenation. In general, the dissolved oxygen can be removed from solution by chemical or physical means. Among physical methods, purging of samples with an inert gas (usually nitrogen or argon) is commonly used. The time required for effective removal of oxygen varies with the gas flow-rate, solution volume and geometry of the process glass, and lasts 10-15 min, thus representing the most time-consuming step in the entire analysis (13). Although physical methods of deoxygenation are quite effective, they have a number of disadvantages. Namely, the oxygen could diffuse back into the system through tubing and joints, and it is difficult to deoxygenate more than one sample at the same time (14, 15).

Other methods for oxygen removal include the use of electrochemical or chemical (zinc) scrubbers, nitrogen-activated nebulizers, and chemical reduction (12). Chemical reduction can be extremely effective. It is carried out by addition of a substance to the tested solution that rapidly reacts with oxygen. In the choice of a substance for chemical reduction, it is important to avoid reaction between the reductant and the target analyte. The most common reductant reported in the literature is sulfite ion (11, 12, 16). In its application it should be kept in mind that in polarography its application is limited to the solutions of pH greater than 8, due to the appearance of polarographic waves (17). Beside sulfite ion, ascorbic acid is also used for oxygen reduction (18).

This study compares different methods of deoxygenation prior to the chronopotentiometric determination of imidacloprid on glassy carbon electrode. The investigation included physical deoxygenation with nitrogen purging, chemical deoxygenation by addition of sulfite ion to the tested solution, as well as combination of physical and chemical methods. The objective was to simplify and shorten the procedure of oxygen removal as much as possible, in order to perform chronopotentiometric determination of imidacloprid by obtaining a high and reproducible signal of the analyte.

EXPERIMENTAL

Reagents and solutions

All chemicals used were of analytical grade purity. Double distilled water was used throughout. Imidacloprid stock solution (0.4 g/dm^3) was prepared by dissolving an appro-

priate amount of the reference standard of imidacloprid (Dr. Ehrenstorfer, Augsburg, Germany) in double distilled water. Britton-Robinson buffer, prepared from equimolar 0.04 mol/dm^3 stock solutions of orthophosphoric, boric and acetic acids was used as a supporting electrolyte. All three acids were purchased from Lach-Ner, Brno, Czech Republic. The appropriate pH value (7.5) of the buffer was adjusted by 0.2 mol/dm^3 sodium hydroxide solution (Lach-Ner, Brno, Czech Republic). The saturated solution of sodium sulfite (230 g/dm^3) was prepared immediately before the analysis by dissolving an appropriate amount of sodium sulfite (Centrohem, Stara Pazova, Serbia) in double distilled water.

Apparatus

All chronopotentiometric investigations were performed on a stripping analyzer with three-electrode cell. The working electrode was a glassy carbon disk of total surface area 7.07 mm^2. A platinum wire (φ=0.7 mm, l=7mm) served as a counter electrode, and the reference electrode was Ag/AgCl (KCl, 3.5 mol/dm^3). All values of the potential were shown versus Ag/AgCl. Electric stick stirrer was also an integral part of the three-electrode system. The analyses were performed in special glass vessels (volume of 50 cm^3) with tapered bottom. The pH values were measured with a digital pH meter model MA 5705 (Iskra, Kranj, Slovenia).

General procedure

The model system, consisting of the supporting electrolyte and imidacloprid was used in all experiments. The Britton-Robinson buffer pH 7.5 was used as supporting electrolyte: 20 cm^3 was pipetted into the process glass, followed by addition of a certain volume of the imidacloprid stock solution. For the chemical removal of dissolved oxygen from the solution, appropriate volume (0.6, 0.8 and 1.0 cm^3) of the saturated solution of sodium sulfite was added to the model system. For the physical deoxygenation, the solution was purged with nitrogen for appropriate time (5, 10 and 15 min), while the solution was constantly stirred. For removing traces of oxygen from nitrogen, the gas was first purged through a pyrogallol solution, and then through the Britton-Robinson buffer, to saturate gas stream in order to prevent evaporation of the sample. Nitrogen was allowed to escape through a tube that was immersed in the double distilled water. During nitrogen purging the working electrode was kept in a special glass with double distilled water. When a combination of nitrogen purging and reduction with sulfite ion was applied for oxygen removal, 0.4 cm^3 of saturated sodium sulfite solution was added to the model system, the apparatus was blanked, and the solution was purged with nitrogen for 5 min.

After removing the oxygen, the solution was stirred for 15 s, followed by a quiet period (10 s), and the analysis was performed. For comparison, the deoxygenated supporting electrolyte was used as a blank. The chronopotentiogram was recorded in a potential range from -0.91 V to -1.42 V. All experiments were performed at room temperature (23±2^{o}C).

RESULTS AND DISCUSSION

In chronopotentiometry, the signal of the imidacloprid was not noticeable due to multitude of peaks that occurred on the chronopotentiogram owing to the oxygen reduction on the working electrode. As a consequence, the final potential of the analysis of -1.42 V was inaccessible, even by applying the maximum current of -50 μA, indicating that the dissolved oxygen had to be removed from the solution.

Preliminary experiments were focused on the background chronopotentiograms recorded for the blank after applying chemical deoxygenation by adding different volumes (0.6, 0.8 and 1 cm^3) of saturated sodium sulfite solution. Further background chronopotentiograms were recorded for the blank deoxygenated by purging nitrogen for 5, 10 and 15 min. The experiments were performed in triplicate for each value. In the case of chemical method, the addition of 0.8 cm^3 of saturated sodium sulfite solution yielded the best appearance of the chronopotentiograms. Namely, the recorded chronopotentiogram was sharp with no-signal baseline.

After the addition of imidacloprid to the blank, the analytical signal appeared at the potential of -1.2 V (9). After prolonged standing of the tested solutions in air, or after multiple addition of solution of imidacloprid to the process glass, only 15 s of stirring prior to the recording was enough to perform the analysis. The applied concentration of sulfite ion was enough to maintain the concentration of dissolved oxygen at a level that did not affect the performance of the chronopotentiometric analysis.

When dissolved oxygen was removed by nitrogen purging, 10 min was sufficient to that purpose, and a longer time did not contribute to a better appearance of the background chronopotentiogram. However, further deoxygenation in duration of 2 min was required because of the oxygen creeping in from the outside. The combination of sulfite ion and nitrogen purging (0.4 cm^3 of saturated sodium sulfite solution and 5 min) did not produce satisfactory result regarding the background chronopotentiograms with nitrogen purging shorter than 10 min.

In order to choose a method for oxygen removal aiming the imidacloprid chronopotentiometric determination, analytical signals of 15 mg/dm^3 imidacloprid obtained after applying different deoxygenation procedures were considered. The results are shown in Table 1.

Table 1. Analytical signals of imidacloprid in dependence of the applied method for dissolved oxygen removal

Deoxygenation method	Analytical signal (s)	RSD (%)
Nitrogen 15 min	0.87 ± 0.05*	2.87
Nitrogen 10 min	0.88 ± 0.05	2.84
Nitrogen 5 min	0.58 ± 0.03	2.59
Nitrogen 5 min and 0.4 cm^3 of saturated Na_2SO_3 solution	0.66 ± 0.05	3.79
0.6 cm^3 of saturated Na_2SO_3 solution	0.88 ± 0.06	3.41
0.8 cm^3 of saturated Na_2SO_3 solution	0.90 ± 0.03	1.67
1 cm^3 of saturated Na_2SO_3 solution	0.84 ± 0.05	2.98

*Xmean ± 2SD, n = 3.

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The highest signals were obtained after the addition of sulfite ion and after 10 and 15 min of nitrogen purging, and the lowest after the nitrogen purging for 5 minutes (0.58 s), while a poor reproducibility was observed by applying the combination of nitrogen purging and sulfite ion addition (RSD = 3.79%). By comparing the height and appearance of the signals when different methods for deoxygenation were used, it can be seen that they were practically the same. These results indicate that there was no chemical reaction between sulfite ion and the target analyte. The best reproducibility was achieved by applying chemical deoxygenation with addition of 0.8 cm^3 of saturated sodium sulfite solution (RSD = 1.67%). Thanks to the much easier performance, and short duration, chemical deoxygenation with addition of 0.8 cm^3 of saturated sodium sulfite solution can be accepted as optimal in terms of the reduction of imidacloprid on glassy carbon electrode.

The chronopotentiometric method using optimal deoxygenation procedure was applied for the determination of imidacloprid content in commercial formulations. Commercial formulations containing imidacloprid as an active ingredient were properly diluted with double distilled water, and finally with Britton-Robinson buffer. Imidacloprid was determined by the calibration curve method, and the obtained results are presented in Table 2. The obtained values for the imidacloprid content were in good agreement with the manufacturer specification, indicating that the optimized chemical deoxygenated procedure can be used for the determination of imidacloprid in commercial formulations.

Table 2. Contents of imidacloprid in the commercial formulations determined by the chronopotentiometric method involving the optimized deoxygenated procedure

Commercial formulation	Imidacloprid content claimed by the manufacturer [g/kg]	Imidacloprid content found by chronopotentiometric method with optimized deoxygenated procedure [g/kg]
Confidor 70 WG	700	699.27 ± 10.56*
Imidor 70 WS	700	708.88 ± 8.04

*Xmean ± 2SD, n = 3.

CONCLUSION

Chemical reduction of dissolved oxygen by adding sulfite ion provides the conditions suitable for the chronopotentiometric analysis of imidacloprid. Namely, the reaction between the sulfite ion and dissolved oxygen was almost instant, allowing that in duration of 30 s of stirring the solution, the dissolved oxygen was at a level that enabled the analysis. Thus, conventional time-consuming step of purging of sample with inert gas was avoided. The method was also distinguished by its simplicity, because it required only a saturated solution of sulfite ion, compared to a complicated apparatus when nitrogen was used. By comparing the analytical signals, it was found that sulfite ion did not react with the analyte; the best reproducibility was achieved by adding 0.8 cm^3 of the saturated sodium sulfite solution. Given all stated advantages, the deoxygenation procedure with sulfite ion accompanied with chronopotentiometric analysis can be used as a routine tool for the imidacloprid determination in food and water quality control.

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ПОРЕЂЕЊЕ РАЗЛИЧИТИХ МЕТОДА ЗА УКЛАЊАЊЕ РАСТВОРЕНОГ КИСЕОНИКА: ПРИМЕНА ПРИ ЕЛЕКТРОХЕМИЈСКОМ ОДРЕЂИВАЊУ ИМИДАКЛОПРИДА

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У овој студији поређене су различите методе за уклањање раствореног кисеоника из раствора пре хронопотенциометријског одређивања инсектицида имидаклоприда на електроди од стакластог угљеника. Истраживање је обухватало примену хемијске методе додатком сулфитног јона и физичке методе провођење струје азота кроз узорак у трајању од 5, 10 и 15 мин, као и њихову комбинацију. Поређењем аналитичких сигнала имидаклоприда, хемијска метода показала је скоро исту ефикасност као и конвенционална физичка метода, док је најбоља репродуктивност остварена применом хемијске методе уз додатак 0,8 cm^3 засићеног раствора натријум сулфита. Метода је веома једноставна и може се применити за уклањање кисеоника из раствора пре извођења хронопотенциометријске анализе. Применом хемијске деоксигенације значајно се скраћује трајање хронопотенциометријске анализе имидаклоприда са 15 мин на 1 мин.

Кључне речи: имидаклоприд, сулфитни јон, хемијска деоксигенација.

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