E2-21: Electrochemical detection of herbicides

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The wide application of agrochemicals has become a major contribution to environmental pollution in Sri Lanka. Detection of such environmental pollutants in surface and ground waters would be a necessity in order to investigate the level of pollution. Existing detection methods have several drawbacks such as high cost, derivatization procedures and lack of reproducibility. Amperometric sensors based on chemically modified electrodes provide an alternative approach which would overcome several limitations of existing techniques. This study is based on the use of some metalloporphyrins for catalytic reduction of organochlorine pesticides. Glassy carbon electrodes modified with metalloporphyrin catalysts can selectively determine this class of pesticides. The proposed method of detection is reproducible, sensitive and economical.

The compound, 5,10,15, 20-tetraphenylporphyrinato iron (III) chloride [Fe(III)TPPCl] was purchased from Aldrich Chemical Company and used as received. The Propanil formulation was an agricultural sample obtained from the Department of Agriculture, Sri Lanka. Dichloromethane and acetonitrile solvents were reagent grade, and distilled prior to use. All supporting electrolytes (LiCl, NaCl, KCl) were analytical grade. Electrolyte solutions for all experiments were prepared in mixed solvent systems of acetonitrile and water. Before each experiment, deaeration of the solution was accomplished by spraying with nitrogen. All cyclic voltametric and amperometric measurements were made with a 3-electrode potentiostatic circuit. Glassy carbon (GC), platinum wire and saturated calomel electrodes were used as working, auxiliary and reference, respectively, for all experiments. An Oxford Instruments potentiostat served as the basic electrochemical analyzer. The results were recorded on a Yew Instruments Model 3022 X- Y recorder.

Glassy carbon electrodes were cleaned using alumina slurry on a polishing pad for 30 sec followed by 5 min sonication. Next, the electrode was air dried and dipped into the metalloporphyrin coating solution twice. The solvent was allowed to evaporate before experimental measurements.

Cyclic voltametric studies of Propanil solution prepared in the acetonitrile/water (1:3) mixed solvent system conducted at a metalloporphyrin modified glassy carbon electrode indicate that Propanil can be catalytically reduced at about -0.3 V. Hence, this potential was selected for all steady-state amperometric studies. The current of the modified electrode measured at the pre-determined potential with sequential additions of the Propanil solution is directly proportional to the bulk concentration of the analyte. However, bare glassy carbon electrodes do not result in a significant amperometric response, suggesting the potential utility of metalloporphyrin modified electrodes as an amperometric sensor for Propanil.

Although current responses are little higher at more negative potentials, the potential of -0.3 V was selected as the operational potential of the sensor because several interference species including oxygen may be reduced at higher potentials. On the other hand, lower potentials lead to much lower sensitivities although there are less interference problems.

Optimization of electrolyte is not necessary because all chloride electrolytes give similar amperometric responses. Amperometric experiments conducted at different compositions of acetonitrile and water show that the highest sensitivity is obtained when the composition is 1:3 (acetonitrile:water). This composition is a compromise between the polarity of the analyte molecule and the rate of electron transfer at the modified electrode.

Glassy carbon electrodes modified with Fe(III)TPPCl show a significant electrocatalytic activity towards the reduction of Propanil. This demonstrates the applicability of metalloporphyrin modified electrodes as amperometric sensors for Propanil. The proposed sensor performs best at -0.3 V, in a 0.1 M chloride electrolyte dissolved in the water / acetonitrile (3:1) mixed solvent system.