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Chemically Modified Electrodes for Detection of Pesticides

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1. Introduction

Environmental problems and their control have received a great deal of interest and publicity, and the number of pesticides used in agriculture and other applications has been steadily increasing. Environmental scientists are concerned with reliable means for detecting these compounds. Although many advances have been made in this area in recent years, much is yet to be accomplished. Chemistry plays a vital role in environmental protection, and analytical chemistry must meet the challenge of providing qualitative as well as quantitative characterization of pesticides. It has already been warned that some organic and inorganic compounds have harmful effects at substantially lower levels than previously suspected (1). Thus, there is a great necessity for new analytical methods with better precision, accuracy, sensitivity and selectivity. These methods must not be prohibitively expensive and, ideally, could be adapted for measurement in the field.

Existing analytical techniques have limitations when used for environmental monitoring. X-ray and electron diffraction, mass spectrometry, activation analysis, and spectral laser methods are not only sophisticated and expensive, but also require specially trained personnel for proper operation of instrumentation. Although gas-liquid chromatography (GLC or GC) has been used with its variety of sensitive and selective detectors, the technique is limited to volatile compounds (2). Non-volatile compounds are commonly derivatized prior to gas chromatographic detection to increase their volatility. High performance liquid chromatography (HPLC) is useful for non-volatile samples (3), but commercially available detectors are limited in sensitivity and/or selectivity.

A variety of electroanalytical methods have been widely employed for detection of pesticides at bare electrodes (4-7). Drawbacks of bare electrodes have been overcome by the use of electrodes whose surfaces are modified with specific functionalities (chemically modified electrodes or CMEs). This paper summarizes analytical capabilities of electrochemistry for detecting pesticides in the environment. The discussion will be mainly focused on electrochemical detection of pesticides at metalloporphyrin modified electrodes (MPEs). An introduction to CMEs and metalloporphyrin electrochemistry will also be included. Furthermore, the application of modified electrodes for detection of pesticides and the suitability of electrochemistry in conjunction with liquid chromatography (LCEC) for separation of environmental samples followed by detection of pesticides will be discussed.

2. Electrochemical methods

2.1 Electroanalytical chemistry

Electroanalytical techniques are those which show a quantitative relationship between the magnitude of an electrical quantity and the bulk concentration of the analyte. The electrode in solution is, in many respects, a transducer between chemical and electrical entities. The role of the electrode is either to monitor species in solution or to generate new species. Electroanalytical methods are categorized as either static or dynamic. Static methods (e.g.: potentiometry) involve measurements of potential difference at zero current without changing the Nernstian equilibrium at the electrode-solution interface. In dynamic techniques (e.g.: voltammetry, amperometry), the system is disturbed by electrical excitation signals consisting of a variety of potential or current programmes, and the resulting response is measured (8).

Electroanalytical methods have received much attention in the area of environmental chemistry, because they are sensitive and selective. Further, instruments used are relatively simple to operate and potentially portable. Many electroanalytical techniques are used for the analysis of water, atmosphere, solid and food materials. Table I summarizes common electroanalytical techniques and their detection limits (2, 8-10). However, the selection of a particular method and its exact detection limit depend on the nature of the analyte and the sample.

Method	Concentration/mol dm ⁻³
Potentiometry	10 ⁻² – 10 ⁻⁴
Conductometry	10 ⁻³ – 10 ⁻⁵
Polarography	10 ⁻⁴ – 10 ⁻⁶
Cyclic voltammetry	10 ⁻⁴ – 10 ⁻⁶
Rotating disk voltammetry	10 ⁻⁴ – 10 ⁻⁶
Steady state amperometry	10 ⁻⁵ – 10 ⁻⁷
Amperometry with flow injection analysis	10 ⁻⁷ – 10 ⁻⁹
Square-wave and differential pulse voltammetry	10 ⁻⁶ – 10 ⁻⁸
Anodic stripping voltammetry with a solid electrode	10 ⁻⁸ – 10 ⁻¹⁰
Anodic stripping voltammetry with a hanging drop electrode	10 ⁻⁷ – 10 ⁻⁹
Electrochemistry coupled with liquid chromatography (LCEC)	10 ⁻⁹ – 10 ⁻¹²

Table I. Common electroanalytical techniques and their concentration range of detection.

2.2 Electrocatalysis

For a molecule to be directly investigated electrochemically, it must have an electroactive group (electrophore) for reduction or oxidation. In certain cases, the molecule of interest (analyte) shows electroactivity beyond the available potential range of the working electrode, as a result of sluggish kinetics. The rate of electron transfer of such reactions can easily be increased by means of electrocatalysis, a process in which the introduction of a catalyst decreases the reduction (oxidation) potential of the analyte by decreasing the

overpotential, or alternatively, increases the reduction (oxidation) current. Electrocatalysis can also be used to avoid interference from dissolved species (8, 9).

Homogeneous electrocatalysis utilizes the catalyst and the analyte in the liquid phase, while heterogeneous catalysis utilizes the catalyst in the solid phase, usually as a coating on the electrode surface. There are two main types of electrocatalysis, redox and chemical catalysis. Chemical catalysis is a complicated process which involves the electrochemical generation of the active form of the catalyst. Transient formation of an adduct between the active form and the analyte would then take place. The chemical bond thus formed is cleaved yielding product(s) and regenerating the starting form of the catalyst (11).

2.3 Chemically modified electrodes (CMEs)

The concept of CMEs originated in the mid-70's when electrochemists sought to control the chemical nature of electrode surfaces (12, 13). CMEs are different from classical (bare) electrodes in that the electrode surface is altered by immobilizing molecules in a rational fashion so that the electrode thereafter displays new properties. Drawbacks of bare electrodes, such as adsorption of molecules or ions, unpredictable surface reactivity and sluggish kinetics can be overcome by modifying the electrode surface (14). The molecules to be immobilized can be selected on the basis of known and desired properties, for instance, electron transfer mediator catalysts, functionalities which scavenge trace molecules or ions for preconcentration, photosensitizers, corrosion inhibitors and outer sphere electron transfer agents.

The principal routes to the immobilization of substances are, chemisorption, covalent bonding, multimolecular layer deposition and electropolymerization (14). If a catalyst is immobilized on an electrode surface, it is essential to understand the electrochemistry and reactivity of the catalyst in order to utilize it in electrochemical detection. The following section explains the electrochemical behavior of metalloporphyrin catalysts in aqueous and nonaqueous media, and importance of MPEs in the detection of pesticides.

3. Electrochemistry of metalloporphyrins

Metalloporphyrins and their derivatives are well known nucleophiles capable of displacing the halide ion in alkyl and aryl halides yielding the corresponding alkyl or aryl metal-nucleophile complex (15-17). The exact mechanism of the nucleophilic substitution seems to depend on the type of substrate and the metal ion. This process can be catalyzed by supplying electrons via electrochemical, photochemical, or by several solvated ions of alkali metals dissolved in liquid NH_3 , or by other electron-transferring agents (18).

Commonly available metalloporphyrins are insoluble in aqueous media, requiring nonaqueous solvents for investigation of porphyrin electrochemistry (19). Metalloporphyrins usually show four electrochemical processes when the last reduction is observed [usually more negative than -1.4 V vs. saturated calomel electrode (SCE)] (20). Cyclic voltammetric studies of cobalt tetraphenylporphyrin [Co(II)TPP] in CH_2Cl_2 shows the expected reduction peaks including the catalytic reductive dehalogenation of the solvent, CH_2Cl_2 , a reaction that had not been previously thought of (15).

Although metalloporphyrins have been known to catalyze the reduction of organic molecules containing halogen groups, early studies of catalytic chemistry of organohalides was limited to nonaqueous media at bare electrodes due to solubility problems of many commonly used metalloporphyrins. The behavior of metalloporphyrins in aqueous solution

was later studied by modifying the bare electrode surface with a metalloporphyrin coating, or alternatively, modifying the surface with a foreign matrix (e.g.: polymer) in which metalloporphyrins are immobilized. Electrodes prepared in this manner have shown substantial differences from the solution behavior (15).

Elliot and Merrese introduced the concept of using MPEs for investigation of catalytic properties for the reduction of organohalides (21). They conducted a series of cyclic voltammetric experiments at meso-tetra(p-aminophenyl)porphyrinatoiron(III) modified pyrolytic graphite and glassy carbon electrodes (GCEs) in dimethyl formamide (DMF). The overpotential for the reduction of benzyl bromide, triphenylmethylbromide and hexachloroethane is decreased in the presence of the metalloporphyrin showing that it is an effective catalyst for the reduction of organohalides. During this process, the surface-bound metalloporphyrin is electrochemically reduced to the formal Fe(I) oxidation state when the potential is scanned, followed by nucleophilic substitution. The demonstration of the catalytic electrochemistry of metalloporphyrins at modified electrode surfaces stimulated the development of electrocatalytic detection schemes for organochlorine pesticides. However, this procedure was not employed to develop electrochemical sensors until recently.

4. Chemically modified electrodes for pesticide detection

4.1 General aspects of environmental monitoring

Atomic absorption spectrophotometry is commonly used for monitoring inorganic pollutants, including pesticides which contain heavy metals. In addition, piezoelectric crystals coated with a variety of selective and sensitive substances for the determination of air pollutants including gasses, explosives and pesticides continue to receive attention of environmental chemists (22, 23). Detection procedures for organic and organometallic pollutants, in particular agrochemicals, based on modified electrodes were limited until the late 1980's, although several direct electrochemical determinations had been reported (24). Among them, the use of polarographic methods for the determination of metal containing dithiocarbamate pesticides and organo-tin fungicides demonstrated the potential applicability of electrochemical methods for the detection of pesticides (25).

Differential pulse and square wave modes of polarography have been applied to increase the sensitivity of detection of classical polarography. Nevertheless, the inapplicability of the dropping mercury electrode for steady state amperometric and LCEC measurements has limited its popularity. Mercury coated and amalgamated electrodes have solved this complication, yet maintaining the advantages of the mercury surface. For such investigation, differential pulse mode is commonly used as it is more sensitive than other modes. In this connection, the possibility of using mercury film electrodes for characterization and detection of triphenyltin acetate, an organo-tin molluscicide, had been attempted (26). The detection conducted by differential pulse anodic stripping voltammetry showed that the lower detection limit was 2.5×10^{-9} M. This detection limit was at least an order of magnitude lower than that of other available techniques such as liquid chromatography and differential pulse polarography. However, the use of heavy metal containing environmental pollutants has significantly decreased over the last decade due to environmental and health problems, and consequently development of detection procedures for organometallic pesticides has not been of high priority in recent days.

Application of electrochemical techniques for environmental monitoring, in particular, for the detection of organic pollutants and toxic gases is becoming increasingly popular due to their desirable characteristics (27, 28). The use of modified electrodes with various electrochemical modes has drawn the special attention of environmental scientists because they offer unique advantages (29, 30).

4.2 Detection of pesticides

Brand and Fleet reported the use of mercury coated platinum wires as voltammetric sensors for the detection of dithiocarbamate pesticides (sodium salt) in the late 1960's before extensive research on "modified electrodes" was begun (31). Later, preliminary investigation on the detection of sulphonyl ureas, a new class of herbicides useful for controlling broadleaf weeds, and s-triazine herbicides such as atrazine, prometryne and simazine, with mercury coated GCEs have been reported (32, 33). The detection schemes developed for these two classes of herbicides based on differential pulse polarography at coated GCEs resulted in a lower detection limit of 10^{-8} M at low pH values. It is impossible to use bare electrodes for the above detection because no reduction wave appears even in a solution of 10^{-4} M herbicide (32). In addition to mercury film electrodes, carbon paste electrodes later became attractive due to the fact that they can easily be modified with any material, by mixing with carbon paste (34).

Potentiometric sensors with modified electrode surfaces for environmental analysis include polyvinylchloride (PVC) coated aluminium wires and piezoelectric quartz crystals modified with crown ethers (e.g.: dibenzo-30-crown-10 or DB30C10) for detecting the herbicides, diquat and paraquat (35, 36). The modified piezoelectric crystal demonstrated the use of ion-selective electrodes as sensors for diquat and paraquat in the gas phase while the PVC coated electrode was employed for potentiometric titrations in solution.

4.3 Pesticide detection with biosensors

A biosensor is an analytical device which converts a biological response into an electrical signal. The term 'biosensor' is often used to cover sensor devices used in order to determine the concentration of substances and other parameters of biological interest even where they do not utilize a biological system directly. Among various kinds of biosensors employed for environmental monitoring, electrodes modified with microorganisms (biofilm electrodes) were first introduced for the analysis of waste water samples. An oxygen electrode whose surface was modified with bacteria or yeast biofilms was used as an amperometric sensor to monitor the oxygen consumption in enzymatic reactions of microorganisms (biochemical oxygen demand or BOD) (37, 38). These BOD probes had a life time of several weeks. After realization of advantages of biosensors, potentiometric and amperometric biosensors with different types of modifiers were designed to detect pesticides in water samples (39-41). There is a vast number of publications devoted to this aspect to date.

5. Metalloprophyrin modified electrodes (MPEs) for detection of pesticides

Although electrodes modified with various reagents had been constructed for detection of pesticides, not much attention had been paid on metalloprophyrins as electrode modifiers. The use of MPEs for detection of clinically important compounds (42) and inorganic ions

(43) as well as the well understood catalytic reduction mechanism of organohalides by metalloporphyrins opened a new era of using MPEs for electrochemical sensing of pesticides. Our research group has been expanding the use of electrodes modified with metalloporphyrins and other reagents for the development of novel detection schemes for pesticides, in particular, those which are used on rice cultivation, herbicides and other compounds of environmental significance.

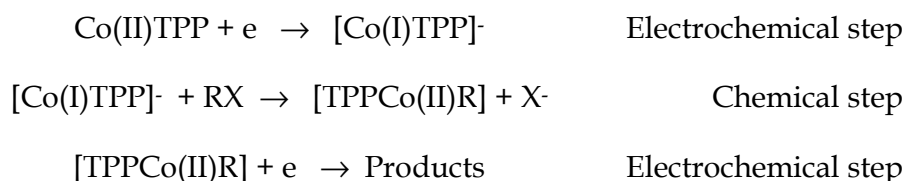
5.1 Electrochemical detection of halogenated, aromatic substances

As indicated earlier, electrochemistry of a metalloporphyrin in nonaqueous medium is different from that in the solid phase in the form of a coating in aqueous or mixed aqueous systems. The notable difference is that the electroactivity of the conjugated system is not evident in aqueous medium, and hence the redox chemistry of the metal center is predominant. Cyclic voltammetry obtained at the tetraphenylcobalt(II) [Co(II)TPP] modified GCE in a mixed aqueous/nonaqueous solvent system (CH₃CN/H₂O; 1:3) shows the reduction of Co(II)TPP to [Co(I)TPP]⁻¹ at -0.34 V vs. SCE (15). Similar behavior is observed with Fe(III)TPP modified GCEs as well. GCEs are more suitable for electrochemical detection of substances in aqueous solution because noble metal electrodes such as Pt, Pd and Au in the absence of any analyte show complicated electrochemistry. Hydrogen adsorption, hydrogen desorption, formation of surface oxide and reduction of the oxide are the main complicated processes (9).

Organochlorine herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA), are commonly used for post-emergence control of annual and perennial broadleaf weeds in cereals, rice and several other plants. There are several metabolic pathways for 2,4-D and MCPA in the environment including hydroxylation, ring opening and cleavage of the acid side-chain. The toxicity level of these two herbicides for mammals is in the order of 10⁻⁴ M (several hundred ppm) (44).

The addition of 2,4-D to the electrolyte solution consisting of the Co(II)TPP modified GCE has produced dramatic changes in the voltammogram. Two reduction peaks were observed at -0.15 V and -1.20 V (vs. SCE) during the complete potential scan. The reduction at -1.2 V is 0.15 V more positive than the potential required for the reduction of 2,4-D at bare GCE, demonstrating the catalytic activity of Co(II)TPP. This response is probably associated with the direct reduction of the carboxylic acid group in the herbicide molecule. It would be very difficult to obtain accurate quantitative measurements at such a negative potential at bare electrodes as it is very close to the hydrogen evolution potential. Several interferences, including dissolved oxygen, would be reduced at potentials less negative than -1.2 V, disqualifying the second reduction at the modified electrode for chemical analysis. Thus, the first reduction peak has been explored for quantification of 2,4-D.

Additional electrochemical and controlled experiments conducted at the Co(II)TPP modified GCEs suggested the following mechanism for the first catalytic reduction of 2,4-D at -0.15 V (46).



A similar mechanism is suggested for electrodes modified by other metalloporphyrins, where the metal is reduced from a higher oxidation state to a lower value followed by chemical reaction to form a metal-porphyrin adduct. The last step of the mechanism is the electrochemical reduction of the adduct to form various products. The identification of the products is not necessary for quantitative determinations because the concentration of the analyte depends on the catalytic current generated at the electrode surface.

Both Co(II)TPP and Fe(III)TPPCL modified GCEs operating at a constant potential demonstrated the utility of MPEs for amperometric detection of 2,4-D. The calibration curves obtained at the modified electrode showed a linear dynamic range from 2×10^{-6} M to 1×10^{-5} M (45). Amperometric experiments for 4-chlorophenoxyacetic acid (4-CPA), structurally similar to MCPA, gave a similar linear dynamic range, sensitivity and a lower detection limit. Fe(III)TPPCL modified electrodes were found to be more stable than Co(II)TPP electrodes, but the sensitivity was lower. Successful detection of 2,4-D and 4-CPA by MPEs has extended this methodology for the detection of organochloro pesticides such as propanil, endosulfan and MCPA (46-49). Additionally, it has been shown that MPEs have the ability for selective electrocatalysis of bromo-substituted aromatic substances depending on the position of substitution (50). Another step that has been taken further towards real application in the field of pesticide detection is the use of MPEs to determine the levels of propanil in simulated rice field environment by amperometry (51) and to monitor the activity of propanil by cyclic voltammetry (52). Electrodes modified with free base porphyrins do not produce significant current response in these detections proving the necessity of a metal ion at the center of the porphyrin molecule for electrocatalysis of halogenated aromatic hydrocarbons. Detection limits of steady state amperometric procedures can be further improved by flow injection analysis followed by amperometric detection at least by one order of magnitude (15).

5.2 Electrochemical detection of dalapon

The sensitivity and the limits of detection usually depend on various factors, such as type of the analyte, nature of the modifying agent and method of modification. Co(II)TPP and Fe(III)TPPCL modified GCEs are found to be more sensitive to aromatic analytes. The detection limit of 2,2-dichloropropionic acid (Dalapon), a general use herbicide, was about two orders of magnitudes lower than that of 2,4-D and 4-CPA (45).

Although metalloporphyrins are good catalysts for reduction of organohalides, thick coatings can prevent the charge (electron) transfer between the electrode surface and the solution as metalloporphyrin molecules can insulate the surface. Thin coatings do not insulate the surface, but they are easily dissociable due to the catalytic reaction with organic compounds dissolved in solution leaving almost a bare electrode. Thus, electrodes modified with thin coatings would not have a long life time, and the coatings of moderate thickness should thus be used as a compromise. Coatings prepared by droplet evaporation technique give a less reproducible response compared to those prepared by dip coating. The thickness of the coating prepared by the dip coating method can be further decreased, if needed, by polishing the modified electrode. This process would eliminate weakly bound porphyrin molecules, and electrodes obtained after polishing have given a higher sensitivity for the analyte.

6. Detection of pesticides by other chemically modified electrodes (CMEs)

Attempts have been taken to explore the possibility of using different types of CMEs for detection of pesticides/agrochemicals. GCEs modified with stearic acid has provided an amperometric sensor for the detection of paraquat, the active ingredient of the herbicide Gramoxone, with a minimum detection limit 6.4×10^{-4} M (53). Another type of modified electrodes is modified carbon paste electrodes where the modifier is incorporated into carbon paste during its preparation. It has been reported that amperometric determination of MCPA at the MnO_2 -modified carbon paste electrode results in a very low detection limit of 0.20 ppm. Further, the application of the proposed method for quantitative analysis of MCPA formulations has provided reliable results demonstrating the use of CMEs in real applications (54).

7. Application of chemically modified electrodes in liquid chromatographic detection

In spite of the sensitivity of electroanalytical techniques, they cannot be directly utilized in analyzing real environmental samples, which are usually in a complex matrix of several different components. However, the combination of electrochemistry and liquid chromatography (LCEC) provides very selective and sensitive measurements for environmentally important compounds, for example pesticides, with the aid of chromatographic separation. Consequently, several reports have recently appeared on the application of LCEC techniques for detection of pesticides (55 – 57). Nevertheless, LCEC has yet to fulfill its potential for the analysis of pesticides with CMEs.

8. Conclusion

Monitoring current levels of environmental pollution requires more specific, sensitive and accurate measurements. Existing analytical techniques have several drawbacks, and consequently, electroanalytical techniques attract environmental chemists due to their desirable properties. However, electrochemical detection for environmental monitoring with CMEs is still in its early stage. Polarographic determination of herbicides at mercury film coated electrodes and amperometric detection of organic pollutants with bio-film modified electrodes are among the few established electrochemical techniques. Furthermore, application of MPEs for the detection of pesticides containing halogens has been successful due to the reductive dehalogenation reaction catalyzed by metalloporphyrins.

The use of MPEs as amperometric detectors for pesticides after liquid chromatographic separation of environmental samples (LCEC) would be possible in future. Furthermore, the use of electrodes modified with polymers, biological materials as well as other functionalities for detection of pesticides using LCEC techniques will be a promising research area.

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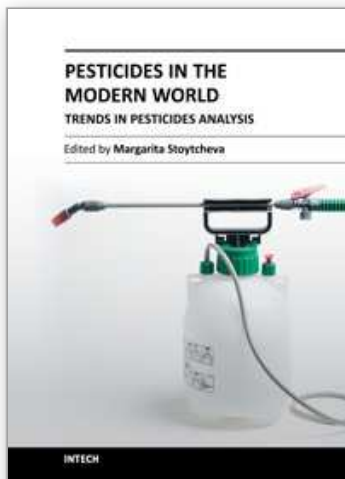
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The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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