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Polarographic and Voltammetric Behavior of Chloropyrifos and Its Determination in Some Water and Plant Samples

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بسم الله الرحمن الرحيم

United Arab Emirates University
Faculty of Science

Polarographic and Voltammetric Behaviour of Chlorpyrifos and its Determination in Some Water and Plant Samples

A Thesis

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Arabic Summary

Abbreviations

DCP	-	Direct-Current Polarography
SCE	-	Saturated Calomel Electrode
M	-	Molar (mol/L)
DPP	-	Differential Pulse Polarography
DP-CASV	-	Differential Pulse-Cathodic Adsorptive Stripping Voltammetry
CP	-	Differential Pulse Polarography
DME	-	Dropping Mercury Electrode
HMDE	-	Hanging Mercury Drop Electrode
CV	-	Cyclic Voltammetry

Abstract

ABSTRACT

Chlorpyrifos is a member of the organophosphorus class of insecticides. This class of insecticides has become one of the most widely under groups of pest control chemicals. Early organophosphorus compounds that were found to be efficacious for insect control and thus brought into widespread use, e.g. Chlorpyrifos, Parathion and Malathion. The broad-spectrum insecticidal properties of Chlorpyrifos indicated that it possessed substantial commercial potential to use against a wide variety of important arthropod pest via a number of commercialized products. Therefore, it is employed in a wide variety of agricultural and specially pest control scenarious and other arthropod pests threatening production of fiber and maintenance of human health. This thesis involves the polarographic and voltammetric behaviour of Chlorpyrifos at the mercury electrode surface. The work was developed for application of the differential pulse-polarography (DPP) and cathodic adsorptive stripping voltammetry (DP-CASV) for determination of Chlorpyrifos in some water samples and in tomato plant.

Chapter I of the thesis includes the environmental impact, sequences for pesticide residue analysis and a literature survey about the preconcentration and analysis of organochloro and organophosphorous pesticides. Also, the objective of this work is included.

The experimental part of the thesis is presented in Chapter II. It includes the chemicals and materials used, the methods of preparation of the various solutions and the methods of preparation of the tested

compound in various water samples. The instruments used for polarographic and voltammetric analysis are included. The general procedures for polarographic and voltammetric analysis as well as, for the extraction of the insecticide from water and plant samples were presented.

In Chapter III the differential pulse polarographic (DPP) behaviour of Chlorpyrifos (CP) was investigated over a wide range of pH (pH 1.8-10.1). CP compound displays a well resolved cathodic reduction peak at -1.2 V vs Ag/AgCl (pH 3.2). This peak is probably corresponding to the reduction of the $\rangle C = N -$ centre of the pyridyl moiety. The effect of solution and operational parameters on the sensitivity of the DPP peak was carefully examined in order to select the optimum conditions for determination of the CP compound. Under the optimum conditions the reduction response gives a linear calibration curve over a concentration range of 9.70×10^{-7} - 6.92×10^{-6} M and the detection limit was found to be 8.7×10^{-7} M. The effects of some diverse metal ions, anions and other organophosphorus insecticide on the determination of CP compound were studied. The applicability of DPP for determination of the CP insecticide in the commercial sample as well as in some irrigation water (treated waste water and underground water) was detected.

The cyclic voltammetric (CV) and the differential pulse - cathodic adsorptive stripping voltammetric (DP-CASV) behaviour of the CP compound at Hg electrode were presented in Chapter IV. The CV indicates that the oxidized form of the CP compound is strongly adsorbed at the mercury electrode surface, which is the ideal condition to apply the DP-CASV method for trace analysis of the CP compound. Under the

optimum conditions (pH 5.01, 10 mV/s scan rate, 50 mV pulse amplitude, -0.4 V adsorption time and 180-240 s adsorption time) the tested compound was detected down to $1x10^{-8}$ mol/L using DP-CASV method. Also, the method was applied for determination of the CP compound in some water samples (tape water, underground water and treated waste water). The degree of recoveries of the CP prepared in various water samples are in the acceptable range (91-103%) except in case of underground water the degree of recovery of CP is relatively low (76-81%). A method of analysis was developed for determination of CP in tomato tissue, it was found that $2.66x10^{-7}$ mol/L CP is the concentration of CP in tomato tissue and it could be determined down to 0.018 mg CP/kg tomato.

It can be concluded that the Chlorpyrifos compound could be determined using DPP with a detection limit of $8.7x10^{-7}$ mol/L. However, the trace analysis of CP could be possible down to $1x10^{-8}$ mol/L (0.0034 mg/L) using DP-CASV technique.

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NOTE

Besides the work carried out in this thesis, the candidate Ali Saeed Rashed Al-Meqbali pursued postgraduate studies for the partial fulfillment of the M.Sc. degree in Environmental Science in the following topics:

A. Core Courses:

Environmental Science I

Environmental Science II

Environmental Law

Social Impact Assessment

Seminar

Applied Statistics

B. Special Courses:

Environmental Chemistry

Selected Topics in Physical Science

Independent Study in Physical Science

Remote Sensing

Pesticidal Chemistry

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CHAPTER I

Introduction

1.1. Environmental Impact and Significance of Pesticides

1.1.1. Historical overview:

Pests have long been known to man. The "Old Testament" has many references to plagues of locust "eaten by the worms" and the olive "that cast his fruit". There are numerous forms of pests and as many attempted control measures. Formulation prepared from plant extracts e.g., nicotine or simple inorganic compounds were perhaps the earliest forms of pesticides recorded in ancient documents of more than several hundreds of years ago in old centuries (Chau & Biu Lee, 1982). The ability of the xenobiotic compound DDT to control undesirable insects was discovered in 1939. Subsequently, methoxychlor, a DDT analog was also found to be effective against a wide range of insects (Chau & Biu Lee, 1982).

In 1945, the discovery of a plant growth regulator known as 2,4-D phenoxyalkanoic acid opened the door for the discovery of a multitude of similar compounds which are used as herbicides to control undesirable weeds by their selective action on broadleaf plants (Khan & Baderka, 1974). Since then, chemicals for pest control had a dramatic rise in types, number and quantity. Although these chemicals control insects, weeds and other pests and hence increase agricultural products and minimize diseases to human and animals, some can also remain active in the environment for long periods of time, and some can affect the nontarget organisms such as fish and wildlife.

The bioaccumulative tendency and nontarget side effects of such pests could pose a hazard to health and to environmental ecosystem (Robinson, 1973). Thus, the monitoring and surveillance of these chemicals in food and in environment is a necessary and basic step for health protection, environmental assessment and pollution control. The identification, characterization and measurement of the concentration of pollutants in the environment provide not only a better understanding of the extent and effects of pollution, but also of the effectiveness of existing and new pollution control action.

The use of the term pesticides seems to encompass a wide range of materials. The broadest dictionary definition of pest indicates that all organic compounds used against troublesome persons,

on adsorption timesidered (Fowler and Fowler, 1951). The normal usage of such materials involves their direct application to the environment coupled with their biocidal nature and requires that considerable effort to be expanded to understand their impact, movement and transformation in the ecosystem.

Pesticides can be defined as substances that kill or control some unwanted organisms such as insects, fungi, undesirable plants, rodents (rats and mice) mites or nematodes (Chau and Lee, 1982). Therefore, according to the intended targets, pesticides can be more accurately classified into the following groups, namely insecticides, fungicides, herbicides, rodenticides, miticides and nematocides. The first three classes of pesticides are the most widely used.

1.1.2. Types and properties of pesticides:

Pesticides belong to many classes of organic compounds. These are: (i) Organochlorines (chlorinated hydrocarbons) which are resistant to hydrolysis and those that undergo photochemical reaction to form compounds with persistence comparable to or greater than their parent compounds (Oloffs *et al.*, 1972; Goring *et al*;., 1975 and Freeman *et al.*, 1975). (ii) Organophosphates (phosphorothionates, phosphorothiolates and phosphorodithioates) which are much soluble in water and are less likely to accumulate in biological tissue (Georgacakis and Khan, 1971), (iii) Carbamates which are derivatives of carbamic acid (fungicides). Those compounds are relatively easily hydrolized and are not considered an environmental problem due to their low persistence, (iv) Phenoxyalkanoic acid derivatives (herbicides) which are biologically not stable and undergo hydrolysis to yield the parent acid and photochemically are not stable, e.g., roadsides and electrical transmission lines (Zepp *et al.*, 1975; Pionke and Chesters, 1973), (v) Substituted ureas which are the common class of biocides and are moderately unstable, undergoing dealkylation and dearylation fairly readily (Dalton *et al.*, 1966 and Smith & Sheets, 1967) and (vi) Triazines which are biologically and photochemically unstable with considerable persistence (Benyon *et al.*, 1972 and Muir & Baker, 1976).

1.1.3. Transport and movement of pesticides:

Pesticides enter the water from various sources. Edwards (1973) reports major sources to include (i) run-off from agricultural lands,

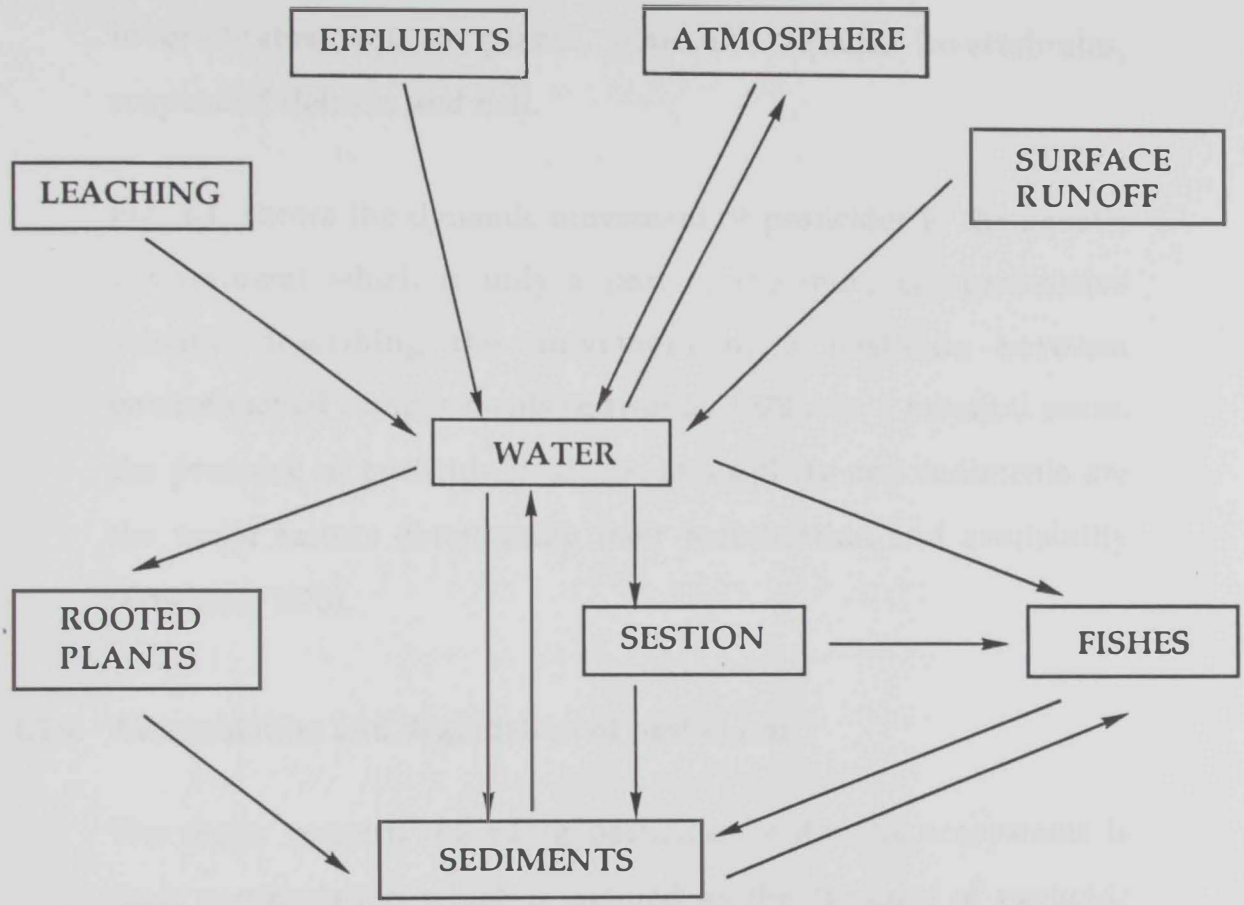


Fig. 1.1 : The dynamic movement of the pesticides in the aquatic environment.

(ii) direct entry from spray operations, (iii) industrial effluents, (iv) sewage effluents, (v) spraying of cattle and (vi) dust and rainfall. In water, the residues and their degradation or transformation products are distributed between the truly dissolved form and those incorporated into sediments, benthic invertebrates, aquatic plants, plankton, aquatic invertebrates, suspended detritus and fish.

Fig. 1.1. shows the dynamic movement of pesticides in the aquatic environment which is only a part of the more comprehensive scheme describing the movement of a pesticide between environmental compartments (Edwards, 1973). In a practical sense, the presence of pesticide in water, atmosphere and sediments are the major factors determining their mobilization and availability (Edwards, 1973).

1.1.4. Accumulation and degradation of pesticides:

The major concern regarding pesticides in aquatic ecosystems is their accumulation which is defined as the "amount of pesticide residue accumulated by an organism by adsorption and, by absorption via oral or other route of entry which results in an increased concentration of the pesticide by the organism or specific tissues" as reported by Benevenue (1976). Biological accumulation, biological concentration, biological amplification and environmental magnification are other terms used for accumulation of pesticides (Edward, 1973). These processes are

controlled by volatility, polarity, partitioning and solubility (Kenaga, 1975).

Mechanisms of bioaccumulation of pesticides were considered to act only via food chain in aquatic ecosystems. Plankton accumulated pesticides from water, which, were then transferred to invertebrates and fish by direct ingestion of the plankton followed by consumption of such fish and invertebrates by higher order carnivores such as fish, marine mammals, birds of human (Edward, 1973). However, Borthwick *et al* (1973) reported that algae contain higher concentrations of pesticides than organisms that are higher in food chain. Therefore, bioaccumulation of pesticides via food chain transfer may explain the accumulation phenomenon.

The bioconcentration kinetics of Chlorpyrifos in guppies were also investigated (Welling & De Vries, 1992). The amount absorbed was calculated from the different rates of the water phase in aquarium with and without fish. The uptake rate was found to be first-order with respect to the exposure concentration. The elimination rate was first order, with respect to the concentration in fish and slightly dependent on the length of the pr-exposure period. The half-life of tissue Chlorpyrifos varied from 31-38 hr and the metabolic breakdown was the only pathway for elimination. A two-component model is proposed to describe the bioconcentration process.

Degradation of pesticides may occur by either chemical or biological processes or by accumulation, oxidation, reduction, hydrolysis,

nucleophilic reactions, reactions involving isomerization, internal cyclization and elimination (Matsumura, 1973 and Paris & Lewis, 1973). Aquatic organisms such as fish can also degrade pesticides by means of biochemical processes resulting from oxidation, hydrolysis and reduction (Edwards, 1973). Pesticides may also degrade in the water column. Edwards, 1973 has shown that persistence of pesticide compounds in water is a function of several environmental factors including solubility, temperature, pH and oxygen conditions. Hill and McCarty (1967) found that most organochlorines degrade under anaerobic conditions except heptachlor epoxide and dieldrin which are persistent. In terms of ease of degradation, ligands was found to be the most degradable followed by heptachlor, Endrin, DDT, TDE, Aldrin, Heptachlor epoxide and Dieldrin in decreasing order (Chau *et al.*, 1982).

Degradation obviously depends upon the nature of the aquatic system investigated. The organophosphorus Chlorpyrifos pesticide added to fresh water at a concentration of 200 $\mu g\ L^{-1}$ decomposed after 7 days only to 6 $\mu g\ L^{-1}$ in water and appeared to have entered the pond sediment (Hurlbert *et al.*, 1970). Therefore, degradation processes and translocations of pesticides are influenced by many factors, e.g. (i) the amount and type of humic substances present, (ii) chemical reactions between herbicides and organic matter and (iii) interactions with sediments and plants.

1.1.5. Toxicology of pesticides:

During the past 25 years it has become apparent that environmental risk assessment cannot be based on acute toxicity data. There is a range of subtle chronic effects on aquatic organisms which may be associated with low doses of pesticides ranging from behavioral aberrations to mutagenesis, and carcinogenesis, or associated with accumulation of residues to levels undesirable to the consumer. The acute toxicity of pesticides to fresh water are expressed in terms of the median lethal concentration (LC_{50}) or median effective concentration (EC_{50}). The median lethal concentration (LC_{50}) and median effective concentration (EC_{50}) of Chlorpyrifos to fresh water invertebrates have been reported by Barron & Wood burn, 1995.

The mode of action of various types of pesticides on target pests has been extensively reviewed by Kohn, 1974 and Matsumura, 1975). The effects of pesticides on nontarget organisms are the main tasks of the environmental agencies and to identify the effect of each of the chemical compounds (Mayer & Hamelink, 1977).

The acute toxicity of Chlorpyrifos has been evaluated in a variety of fresh water, salt water invertebrates wild mammals, fish, reptiles, amphibians and birds species (Barron & Wood burn, 1995). The acute toxicity (LC_{50} or EC_{50}) of Chlorpyrifos to aquatic invertebrates ranges form 0.001 $\mu g\ L^{-1}$ in several species to 12,000 $\mu g\ L^{-1}$ in a rotifer (Snell *et al.*, 1991). Acute toxicity of Chlorpyrifos to the majority of aquatic invertebrates ranges between 0.1 and 10 $\mu g\ L^{-1}$

(Barron & Woddburn, 1975). The acute toxicity of Chlorpyrifos to aquatic invertebrates has also been investigated in pulse exposures and in sediment tests (Key & Fulton, 1993). Exposed grass shrimp to 6 hr pulse exposures of Chlorpyrifos on days 0, 5, 10 and 15 of a 25-days study was investigated by Key and Fulton (1993). LC_{50} s decreased from 0.94 $\mu g\ L^{-1}$ (days 25).

Studies of the chronic toxicity of Chlorpyrifos to microorganisms have included evaluations of population density and functional parameters (Barron & Woddburn, 1995). Lowest observed effect concentration (LOECs) reported for aquatic microorganisms range from 1000 µg/L to greater than 1000,000 µg/L. The EC50 of Chlorpyrifos to photobacteriam phosphoreum assayed in the Microtox system was 46,000 µg/L, whereas the EC50 of the degradation product of Chlorpyrifos 3, 5, 6-trichloro-2-pyridinol (TCP) was 18,600 $\mu g\ L^{-1}$. These results suggest that bacteria are among the most resistant species to Chlorpyrifos. The chronic toxicity of Chlorpyrifos to aquatic invertebrates has been evaluated primarily from effects on reproduction of two sensitive species: the fresh water daphnia daphnia magna and the salt water mysid (Barron & Woddburn, 1995).

1.1.6. Monitoring of pesticides:

The use of simulation models to describe chemical behaviour in aquatic environments is a technique which holds great promise, since it provides a method of combining quantitative and qualitative information to obtain a predictive and descriptive

scenario of the pesticide behaviour. Such models may enable researchers to predict the environmental dynamics of pesticides and hence the duration of associated problems. The development of sound monitoring analytical program in order to process the range of samples, e.g. surface waters, sediments, biological tissues of many sorts air, soil, ground water is of great importance to give reliable answers about the material found in the environment. These developments will be general, for investigative monitoring and compound specific, for routine surveillance. Together with such information, surveillance data on environmental levels should be incorporated into practical models designed to answer the following questions: the qualitative, the quantitative aspects of pesticides determination as well as their life time.

1.2. Sequences for Pesticide Residue Analysis

1.2.1. Sampling, sample handling, storage and preservation:

Sampling is a critical activity for generation of valid data. A practical approach as a part of a quality assurances program is to develop and periodically update sampling guidelines and procedures based on in-house investigation and input from field and laboratory personnel (Chau *et al.*, 1982). Once the samples are properly collected in suitable containers, they should be immediately transported to the laboratory for analysis after immediate addition of preservatives. Sample to be analyzed usually requires some process to render it into a proper form for extraction, e.g., (i) for plant or animal material, it is usually chopped, ground, or blended to facilitate extraction and for a large sample size to provide a homogeneous sample so that a sub-sample can be used for extraction, (ii) for water samples, extraction is performed as the same or with a salt added to facilitate extraction and (iii) sediment samples are mixed, sieved, dried, ground or blended before extraction. However, the sample processing procedures chosen depend on the sample matrix and the parameters to be analyzed.

1.2.2. Preconcentration, isolation and extraction of pesticides:

The pesticide sample cannot be analyzed directly for pesticide residues. Thus, extraction of pesticide is required to isolate the target contaminates from the sample matrix. Extraction in pesticide residue analysis always result in solution of pesticide

residues and sample - co-extractives. Extraction is preferably done as soon as the sample is collected to avoid any possible degradation of pesticides during storage. The commonly used preconcentration techniques in pesticide residue analysis are solvent liquid-liquid extraction, adsorption of pesticides on columns consisting of charcoal, XAD resins or polyurethane foams (El-Shahawi, 1997 and El-Shahawi and Aldhaheri, 1995) followed by desorption with a suitable solvent are the most common techniques. A variety of other extraction methods including blending, shaking, ultrasonic and Soxhlet extraction have been used and shown to be effective on spiked or fortified solid samples. However, the selection of the most suitable extraction procedure for pesticides is dictated by the sample type and extraction method efficiency. For water samples of 1 L or less, extraction can be effected by shaking in a separatory funnel with a suitable organic solvent.

1.2.3. Cleanup of pesticides:

Cleanup is a term used in pesticide residue analysis for the isolation of the target pesticide from interfering co-extractives. The extent of cleanup required prior to final determination depends on the sample type and the selectivity of both the extraction procedure and the method of determination. However, no single universal procedure for cleanup is suitable for all types of sample or pesticides (Chau *et al.*, 1982). The commonly used cleanup techniques in pesticide residue analysis are: (i) liquid-liquid partitioning, (ii) liquid-solid chromatography (column cleanup) employing the most extensively solid adsorbents, e.g., alumina,

silica gel and Florisil, (iii) thin layer chromatography, (iv) chemical cleanup employing acid (strong mineral acid) or alkaline (strong alkali hydroxide, e.g., NaOH) cleanup procedures for only inert pesticides, (v) sweep co-distillation and (vi) gel permeation chromatography.

1.3. Preconcentration and Analysis of Pesticides

It has been stated that every phase of environmental protection control depends on the ability to identify and accurately measure specific pollutants in the environment, i.e. without reliable measurements health effects and relate them to levels of pollution. Therefore, quality control activities are the most important and essential tools to insure the reliability of analytical data.

Chromatographic, titrimetric, photometric and spectrophotometric techniques are most important and widely used for routine analysis of pesticide residue (Ulakhovich & Budnikov, 1992). Wrobez-Zasada *et al.* (1996) reported a simple and accurate method for the spectrophotometric determination of azinphos pesticides in formulation. The method involves application of zero-crossing technique and first derivative spectrophotometric procedure with the aid of internal standard for the spectrophotometric determination of mixture of azinophos pesticides. A new solid-phase extraction procedure employing polyurethane foam column has been tested for the preconcentration of traces of carbaryl pesticides (50-400 ppb) present in water (Rathor *et al* ., 1995). The polyurethane foam plug was extracted with chloroform, the solvent was evaporated and the solid residue was determined spectrophotometrically. The recovery percentage was 73-98% of the tested pesticides in deep well water, river water, rain water and distilled water.

Mathew *et al* . (1995) reported a sample spectrophotometric method for the determination of carbyl in soils and insecticide formulations. The proposed method was based upon the coupling of carbyl with diazotized 2-aminonaphthalenesulfonic acid in alkaline solution to form an azo-dye which has a maximum absorbance at 490 nm. The method suffers no interference from phenol, 1-naphthol and other carbamates. The fungicide fubridazole residue was determined by Sanchez & Gallardo (1994). A detection limit of 0.08 ng ml^{-1} and RSD of 2.3% were the most analytical specification offered by the method. A kinetic spectrophotometric procedure was developed for the determination of propoxur, carbyl, ethiofencarb and formetanate (Garcia *et al* ., 1995).

Diaz *et al* . (1995) reported accurate spectrofluorimetric and enzymatic methods for the determination of Chlorpyrifos in apples based on the inhibition of the acetylcholinesterase enzyme. The method employs a non-fluorescent synthetic enzyme to yield a highly fluorescent product. The method was employed for the analysis of Chlorpyrifos added to apple with recoveries ranged between 91-107%. The detection limit and the relative standard deviation of the method were found equal 13.88 µM and 7.1%, respectively. Simultaneous determination of dithiocarbamates by capillary electrophoresis with diode array detection and using factor analysis was recently reported by Lee *et al* . (1997). Butyl-, diethyl-octyl-, dimethyl and pyrrolidine-1-dithiocarbamates were simultaneously determined by capillary electrophoresis with diode

array detection. These compounds gave linear calibration graphs up to 50 μg ml^{-1} with detection limits in the range 0.1-1 μg ml^{-1}.

Galera *et al* . (1994) reported an accurate method for the analysis of the binary mixture of atrazine and first derivative of the ratio spectra of Chlorpyrifos. Calibration graphs were linear up to 15 μg ml^{-1} of Chlorpyrifos. The method has been applied to determine pesticide formulations, in soils and waters. A fast spectrophotometric determination procedure was described (Khalaf *et al* ., 1996), the method was based on the reaction between p-aminophenol and the phenolic compounds obtained from the pesticides after hydrolysis. The partial least-squares treatment of the spectrophotometry kinetic data provides a simultaneous determination of three carbamate pesticides. Fluorimetric determination of aromatic pesticides in technical formulations was reported by Coly and Aaron (1994). The limit of detection ranged from 0.03 to 20 ng ml^{-1}. The relative standard deviations were between 5.5 and 6.1 % and the mean recoveries ranged from 86 to 116%.

Garcia *et al.* 1996 reported a partial-least squares regression and derivative spectrophotometry procedure for the analysis of the active components in insecticide formulations using diode-array spectrophotometer as chromatographic detector. An IR fibre optic sensor has been developed for the *in situ* monitoring of chlorinated hydrocarbons and pesticides in water (Walsh *et al.*, 1996). The method provides a good performance down to single ppm levels and the technique can be applied to multi-analyte

samples. The analysis of carbyl pesticide in polluted water by micella, stabilized room temperature phosphorescence with sodium sulphite as seavenger. The analytical curve of carbaryl gives a linear dynamic range of $2x10^{-7}$ - $6x10^{-5}$ mol/L and a detection limit of $2x10^{-7}$ mol/L.

Recently, Celichowski *et al.* 1995 reported a convenient titrimetric method for the analysis of dithiocarbamate pesticides in natural water. The method presented for the determination of zinc and lead dialkydithiocarbamates in the presence of tetraalkylthiuram disulphides is based on thiomercurimetric titration. Zinc, lead dialkyldithiocarabamates were determined by titration with p-dimethylaminophenylmercury(II) acetate with Michler's thioketone as indicator. The method was simple, rapid, reproducible and accurate and samples do not require separation or other preliminary stages prior to their analysis of dithiocarbamates in fungicides, rubber and plastic formulations.

Gas chromatography is the most important and widely used instrument for routine pesticide residue analysis (Afghan *et al.*, 1982). Lee and Wong (1995) reported a rapid method for the analysis of five fungicide residues in cucumbers after an automated gel permeation chromatographic cleanup by GC with nitrogen-phosphorus detection. The mean recoveries ranged from 87.9% to 96.5%. Carbaryl and its hydrolysis product, 1-naphthol, were determined simultaneously and in a mixture of other pesticides by reversed-phase high performance liquid chromatography.

Fluorometric detection affords a high degree of selectivity than absorbance detection while providing detection limits of 1.0ng ml^{-1} and 1.4 ng ml^{-1} for 1-naphthol and carbaryl, respectively (Massey *et al.*, 1995). Residual organophosphorus pesticides in foods were determined by accelerated solvent extraction (ASE), gel permeation chromatography and GC-FPD (Obana *et al.*, 1997). Wet samples were determined by the proposed method after mixing with extrelut drying agent. The average recoveries of the tested pesticides were 80-90% and the precision was < 10%.

An improved and sensitive gas chromatographic method has been established for the determination of some dialkylthiophosphates (Lin *et al.*, 1995). The detection limits (signal to noise ratio of s) were in the range 8.3 - 5.6 nM, respectively. The method was applied for the analysis of the thiophosphates spiked in plasma after simple ultrafiltration (Lin *et al.*, 1995). Okumura *et al.* (1995) reported an accurate method for the determination of some carbamate pesticides in water and sediment samples. The carbamates were determined at levels of 0.05-1.00 ng ml^{-1} in water with relative standard deviations of 2.6-22.6% and 10 ng g^{-1} in sediment with 5.0-20.3% relative standard deviation. The detection limits of the tested carbamates in water and sediment were 0.014-0.18 ng ml^{-1}. Microextraction and gas chromatography - mass spectrometry were reported for the simultaneous determination of 60 pesticides in contaminated groundwater sample and a contaminated soil sample (Boyd-boland *et al.*, 1996). Polyacrylate and polydimethylsiloxane coated fibers are used to

extract the analytes from the samples over the concentration range 0.1-100 $\mu g\ L^{-1}$.

Bauerle *et al.* 1995 reported an application of selected ejection isobutane chemical ionization for the determination of pyrethroid insecticides by ion trap GC-MS-MS. A detection limit of 5 ppb was achieved in the determination of atrazine in run-off water from agricultural areas. Extraction and preconcentration are accomplished with a column of macroreticular resin. Separation and quantification of the tested atrazine pesticides were performed by high performance liquid chromatography with a microparticle reverse phase column, good linearly in the range 0-120 ppb was obtained.

Agostiano *et al.* 1983 reported the application of Tenax for the preconcentration and recovery of some pesticides (chlorinated, phosphorated, carbamates and carbonates) and other organic toxicants in water at 0.1 ppb level. Revelation and quantitative analysis were performed by gas chromatography and HPTLC. Tenax was found the most suitable material in comparison with other adsorbents. The retention of 30 commercial pesticides on a porous graphitized carbon column using dioxane and water mixtures as eluents was recently reported by Forgacs & Tibor 1995. The retention capacity of the tested pesticides significantly depended both on their lipophilicity and specific hydrophobic surface area determined by reversed phase thin layer. Analysis of the tested pesticides revealed that the hydrophilicity parameters of

the tested species influence their retention behaviour on the porous graphitized carbon column (Forgacs & Tibor, 1995).

The electroanalytical methods polarography and voltammetry are being used with increasing frequency for the determination of pesticides (Ulakhovich & Budnikov, 1992). The analytical possibilities of voltammetry for the determination of phosphorus and sulphur containing pesticides have been presented. The determination of residual amounts of pesticides lies outside the scope of the direct-current polarography, however, polarographs with pulsed or alternating-current recording of the analytical signal at hanging-drop mercury indicator, most of pesticides can be determined.

Prabhu & Manisankar (1994) reported an accurate method for the determination of endosulfan by stripping voltammetry. The electroreduction and adsorption of endosulfan was studied in aqueous and acetonitrile media. Differential-pulse and square-wave stripping voltammetric techniques at a stationary glassy carbon electrode was used for the analysis of endosulfan in soil samples (Prabhu & Manisankar, 1994). A DC polarographic reduction wave at -1.30 V (SCE) was used for the analysis of alachlor. The data of polarographic, coulometric and preparative electrolysis measurements were found consistent with a reductive cleavage reaction mechanism (Carrai *et al.*, 1992). The peak current is proportional to the concentration over the range $1x10^{-7}$-$1x1x10^{-5}$ M. A polarographic study of the reduction of the herbicide simazine in micellar solutions and oil-water emulsions

was reported by Galvez *et al* . (1993). Using DPP, simazine was determined over the concentration ranges $8.0x10^{-5}$ - $4.0x10^{-5}$ mol L^{-1}. The limit of detection was $2.2x10^{-7}$ mol L^{-1} and the method was applied to the determination of simazine in spiked irrigation water with good recoveries (Galvez *et al* ., 1993).

Mazzei *et al.* (1995) reported an inexpensive procedure for the determination of atrazine in environmental samples and in the risk. Sensitive methods for the determination of the herbicides methoprotyne and terbutryne at nonomolar levels by adsorptive stripping voltammetry at a hanging mercury drop electrode were reported by Pedero *et al.* (1993). The working medium chosen was 0.1 mol l^{-1} perchloric acid, accumulation potential of -0.70 V and -180 s accumulation time were used. The detection limits of terbutryne and methoprotryne were $5.2x10^{-10}$ and $2.4x10^{-9}$ mol L^{-1}, respectively (Pedero *et al.*, 1993).A carbon paste electrode chemically modified with Amberlite XAD-2 resin was used for the determination of paraquet by cathodic stripping voltammetry (Alverez *et al.*, 1992). The proposed procedure exhibited good linearity for paraquet concentration lower than 1.08 μ ml^{-1} with a detection of 0.10 μg ml^{-1}. The method was employed for the analysis of paraquet in river water.

The simultaneous determination of the binary mixtures of heptachlor-endosulfan sulphate, endosulfan-endosulfan sulphate, dieldrinendo-sulfan and dieldrin-endosulfan sulphate were successfully analyzed by differential pulse polarographic (Reviejo *et al* ., 1992). The endosulfan-endosulfan phosphate pair was

determined by allowing the mixture to hydrolyse at pH 11.0. The lower detection limits obtained were: endosulfan-endosulfan sulphate mixture, $4.0x10^{-6}$ and $1.0x10^{-6}$ M, respectively; heptachlor-endosulfan sulphate mixture, $2.0x10^{-6}$ M for endosulfansulphate (Reviejo *et al.*, 1992). Walcarius & Lamberts (1996) reported a rapid, sensitive method for the determination of paraquet and diquet in aqueous media using square wave voltammetry in foodstuffs after digestion in hot sulphuric acid, neutralization and solid phase extraction. The detection limit has been found to be $1\mu g\ g^{-1}$ for both pesticides.

Privman *et al* 1994 reported a sensitive adsorptive stripping differential pulse voltammetric method for the determination of prometrine in soil and water. The relationship between i_p and prometrine concentration was linear in the range $1x10^{-8}$-$11x10^{-7}$ M. The relative standard deviation was 6.5% for n = 5 determinations of prometrine in water and 3.1% for prometrine determination in soil. Adisposal multichannel immunochemical sensor based on the electrochemical transducer was reported for the determination of 2,4-dichloro-phenoxyacetic acid in water was 0.1 $\mu g\ l^{-1}$. The multichannel sensor was potentially suitable for the analysis of several samples and standards using one biorecognition system.

A new method for the simple and inexpensive determination of atrazine was reported by Mazzei *et al* ., 1995. The method was based on the use of a novel, partially disposable, plant tissue bioelectrode which was found sensitive to a variety of non-and polyphenols. The concentration of atrazine in aqueous samples was accurately determined. The method was found suitable for the

analysis of atrazine in environmental and risk areas (Mazzei *et al .*, 1995). Classical DC-polarography and fast scan differential pulse voltammetry (FSDPV) were applied for the analysis of five nitropesticides (trifluraline, pendimethalin, bromofenoxim and fluoroglycofenethyl) at a dropping mercury electrode and at a static mercury drop electrode. The detection limit were found both experimentally and calculated from regression. The nitropesticides in artificially contaminated soils were determined after two or three times extraction with acetone and the recovery was about 96%.

1.4 Aim of the Present Work

Recently, there have been an increasing number of xenobiotic materials entering our environment. Many of them are hazardous to human health and to the ecosystem. Pesticides represent a class of man-made environmental pollutants which also occur naturally in the environment. The presence of these pollutants in the industrial and agricultural waste waters often represents a risk to the environment and cause several health problems to animal and human beings. Indeed, the problem of environmental protection and pollution control has become one of modern man's preoccupations.

One prerequisite for decision making environmental protection and pollution control is the ability to identify and measure these xenobiotic material in our ecosystem. In fact, nearly every phase of environmental protection and pollution control depends upon analytical data. However, it is not sufficient to generate data. These data must be reliable and truly represent the situation. Therefore, an effective quality assurance program is needed to ensure the reliability of data. Suitable analytical methodology is the first consideration in an effective quality assurance program for the generation of reliable data.

Chlorpyrifos is a member of the organophosphorus class of insecticides. This class of insecticides has become one of the most widely under groups of pest control chemicals. Early organophosphorus compounds that were found to be efficacious for insect control and thus brought into widespread use,

e.g. Chlorpyrifos, Parathion and Malathion. The broad-spectrum insecticidal properties of Chlorpyrifos indicated that it possessed substantial commercial potential to use against a wide variety of important arthropod pest via a number of commercialized products. Therefore, it is employed in a wide variety of agricultural and specially pest control scenarious and other arthropod pests threatening production of fiber and maintenance of human health.

Chlorpyrifos is a degradable compound and both abiotic and biotic transformation processes affect its degradation within environmental compartments. The major pathway of transformation involves cleavage of the phosphate ester bond to form 3,5,6-trichloro-2-pyridinol (TCP). Soil and water microorganisms are able to metabolize Chlorpyrifos to some degree and in certain environmental compartments may contribute significantly to the dissipation of Chlorpyrifos.

So far, spectrophotometric and chromatographic techniques have been the most widely used for the determination of Chlorpyrifos. To our knowledge, no electroanalytical methods have been described for the determination of Chlorpyrifos. Thus, the main objective of the proposed work was focused on developing simple and convenient electroanalytical methods for the analysis of Chlorpyrifos in different samples, e.g. treated waste water, underground and tapewater, in pesticidal formulations and plants at a very low concentration range of 10^{-8} to 10^{-6} M without any preconcentration step. Differential pulse polarography (DPP) and differential pulse cathodic adsorptive stripping voltammetry

(DPCASV) at a mercury drop electrode (MDE) and at a hanging mercury dropping electrode (HMDE), respectively were critically employed in the proposed work. The effect of different interfering cations and anions and other pesticides which are generally present in the tested matrixes (water, plants and pesticidal formulations) on the determination of Chlorpyrifos were studied.

CHAPTER II

Experimental

2.1. Reagents and Materials

(A) Solutions of pesticide:

All chemicals used were of analytical reagent grade. The compound under investigation is Chlorpyrifos [o,o-diethyl-o-(3,5,6-trichloro-2-pyridyl)phosphorothioate]. The structure of the tested pesticide is given in Fig. 2.1.

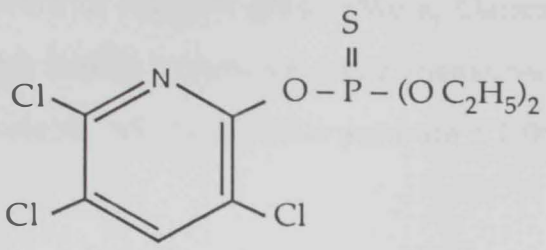


Fig. 2.1. : Structure of Chlorpyrifos.

Malathion, diethy[(dimethoxyphosphos-phinothioyl)thio] butane-dioate and diazinon (o,o-diethyl-o-(3-isopropyl-6-methylpyri-midine) phosphoro-thioate) pesticides were used to investigate their interfering effects on the polarographic and voltammetric determination of Chlorpyrifos.

Stock solutions $1x10^{-3}$ mol/L of each compound were prepared in ethanol. A series of standard solutions of these compounds was prepared by diluting their stock solution with ethanol.

Stock solution of $1x10^{-3}$ mol/L of commercial Chlorpyrifos reagent, which was bought from the market, was prepared in ethanol. Dilute solutions were prepared by diluting their stock solution with ethanol.

(B) Britton-Robinson (BR) buffer solutions:

BR is a universal buffer containing the pH range 2-11. The BR buffer was prepared by neutralizing an acid solution mixture (0.08 mol/L of acetic, boric and phosphoric acids) with 0.02 mol/L NaOH. The BR buffer was brought to constant ionic strength by addition of 0.025 mol/L $NaNO_3$ and adjusted to the desired pH. All chemicals were of reagent grade (Merk, Darmstadt and BDH). The pH's of the buffer solutions were measured with a digital radiometer pH-meter, Model PHM64 accurate ± 0.05 pH unit.

(C) Acid solutions:

Stock solutions of 0.1 mol/L of acetic acid, sulphuric acid, nitric acid and hydrochloric acid were prepared in double distilled water. Dilute solutions were prepared by diluting the stock solution with bi-distilled water to the specific volume.

(D) Metal salt solutions:

Stock solutions of $1x10^{-2}$ mol/L of Mg(II), Ca(II), Cu(II), Zn(II), Pb(II), Cd(II) and Cr(III) were prepared from their analytical grade nitrate salts (BDH chemicals) in double distilled water.

Stock solutions of $1x10^{-2}$ mol/L of sodium salts of SO_4^{-2}, CO, Cl^-, NO_3^-, F^- and I^- were prepared in double distilled water from their Merk and BDH chemicals. Solutions of $K_2Cr_2O_7$ and KCl ($1x10^{-2}$ mol/L) were prepared from the Merk Chemicals by dissolving the required weight in a specific volume of double distilled water.

Dilute solutions of the above solutions were prepared by diluting the stock solution with double distilled water to the specific volume.

(E) Solutions of Chlorpyrifos in some environmental media:

A series of stock solutions of $1x10^{-3}$ mol/L of Chlorpyrifos were prepared by dissolving the required weight in one litre of tap water, treated wastewater and underground water containing 10% (v/v) ethanol. Dilute solutions were prepared by diluting the stock solution by the specific water type containing 10% ethanol. Also $1x10^{-3}$ mol/L of solutions of the commercial Chlorpyrifos reagent in the various type of water were prepared according to the data recorded on the commercial sample. A series of dilute solutions of the later were also prepared.

2.2. Instrumentation

(A) Differential pulse polarographic (DPP) measurements:

DPP measurements were carried out using of Metrohm (Herisau, Switzerland) E-506 polarograph coupled with its 508 mercury stands and/ or 663 VA polarographic stand. Differential pulse polarograms were recorded using a dropping mercury electrode with a mercury height 45 cm and drop time 1.4 s. The pulse amplitude 50 mV, scan rate 4 mV/s and -0.2 V starting potential vs SCE, reference electrode were the conditions used in the most DPP measurements.

(B) Cyclic voltammetric measurements:

A Princeton Applied Research (PAR) Model 264A polarographic and voltammetric analyzer, coupled with a PAR Model 303A mercury standard (HMDE) were employed for cyclic voltammetric measurements. The conditions of measurements were hanging mercury drop electrode (HMDE) as a working electrode with area 0.012 cm^2 versus Ag/AgCl reference electrode and Pt wire counter electrode. Also, 100 mV scan rate, with variable deposition time and starting potential were used to investigate the adsorbability of the tested compounds at the mercury electrode surface. The cyclic voltammograms were recorded on X-Y recorder Model RE0089 (PAR).

(C) Cathodic adsorptive stripping voltammetric measurements:

Cathodic adsorptive stripping voltammetric (CASV) measurements were carried out with a PAR Model 264 voltammetric analyzer in conjuction with a PAR Model 303A HMDE and PAR 305 magnetic stirrer. In CASV the investigated compound is preconcentrated into a hanging drop mercury electrode by adsorption. The measurement step consists of electrolytically stripping the deposited species back into solution by imposition of a potential step as a pulse voltage ramp. The differential pulse mode is used because of its correction for the charging current and commercial availability. The amount of investigated compound accumulated on the electrode surface in addition to the variables of solution, concentration and pH, is also affected by other variables such as deposition time, accumulation potential, scan rate. Instrument setting for differential pulse cathodic stripping voltammetry (unless otherwise stated) were: scan rate 10 mV/s, pulse amplitude 50 mV, pulsed applied at 0.5 s intervals, deposition time 30-60 s (with stirring, unless otherwise stated). Voltammograms were recorded on an advanced X-Y recorder Model RE 0089 after automated deareation of the electrolysed solution.

2.3. Electrochemical Cell

The cell used for the differential pulse polarographic measurements is thermostated Metrohm Cell equipped with three electrode system. This system contained a dropping mercury electrode (DME) as the working electrode, saturated Calomel electrode (SCE) as the reference electrode and a platinum wire as a counter electrode. All measurements were performed at 22 ± 0.5° (unless otherwise stated). Nitrogen was bubbled through the solution in the cell for 20 min to remove oxygen to an undetectable level and the corresponding polarograms were recorded.

A PAR cell (Fig. 1) equipped with hanging mercury drop (working electrode), Ag/AgCl (reference electrode) and Pt wire (counter electrode) was used for cyclic and differential pulse cathodic stripping voltammetric measurements. The area of the hanging mercury electrode was 1.2×10^{-2} cm^2. Nitrogen was bubbled through the solution in the cell for 16 min to remove oxygen and the corresponding voltammograms were recorded. Also, nitrogen was bubbled through the solution in the cell for 2-3 min after addition of the solution of the tested compound before recording the voltammetric curves.

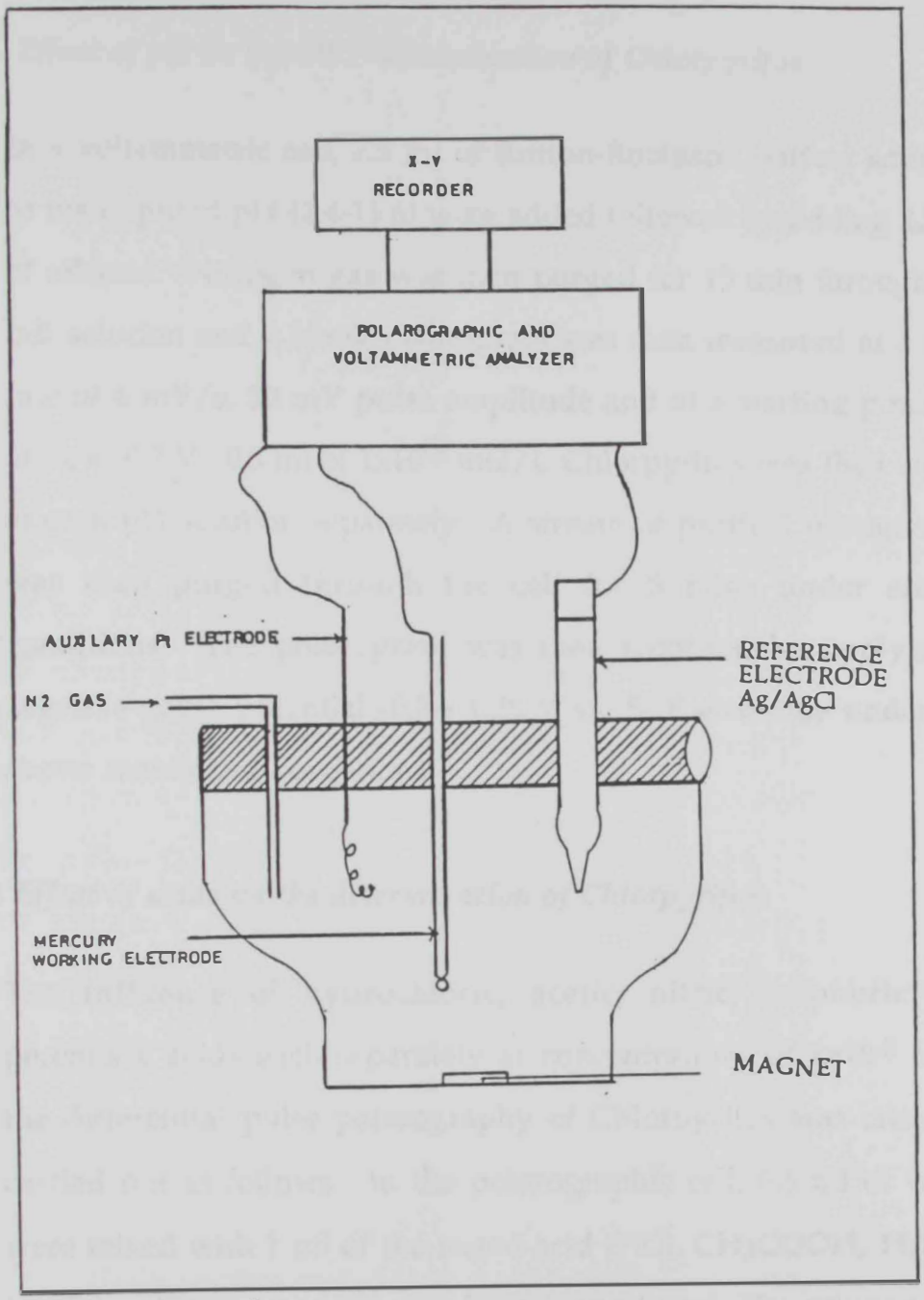


Fig. 2.2. : A PAR polarographic and voltammetric cell.

2.4. Procedures

2.4.1. Experimental Procedures in Differential Pulse Polarography (DPP) of Chlorpyrifos:

2.4.1.1. *Effect of pH on the DPP determination of Chlorpyrifos:*

In a voltammetric cell, 7.5 ml of Britton-Robinson buffers adjusted to the required pH (2.4-11.6) were added followed by adding 2.5 ml of ethanol. Nitrogen gas was then purged for 15 min through the cell solution and a blank polarogram was then measured at a scan rate of 4 mV/s, 50 mV pulse amplitude and at a starting potential of E_s = -0.2 V. 0.5 ml of $1x10^{-3}$ mol/L Chlorpyrifos was then added at each pH solution separately. A stream of purified nitrogen gas was then purged through the cell for 5 mins under stirred conditions. The polarogram was then recorded by applying a negative going potential -0.2 - 1.70 V vs. SCE electrode under the above mentioned conditions.

2.4.1.2. *Effect of acids on the determination of Chlorpyrifos:*

The influence of hydrochloric, acetic, nitric, sulphuric and perchloric acids each separately at concentrations of $1x10^{-2}$ M on the differential pulse polarography of Chlorpyrifos was critically carried out as follows: In the polarographic cell, 6.5 ml of water were mixed with 1 ml of the tested acid (HCl, CH_3COOH, H_2SO_4, HNO_3 or $HClO_4$) and 2.5 ml of absolute ethanol. The solution was deoxygenated by purging N_2 gas for 15 min and the polarogram of the blank was then measured at E_s = -0.2 V vs. SCE and 4 mV. sec^{-1} scan rate and 50 mV_{pp} pulse amplitude.

To the test solution, add 0.5 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) and pass nitrogen through the solution cell for 15 mins and measure the polarogram under the same experimental conditions of the blank.

2.4.1.3. ***Effect of ethanol concentration on the determination of Chlorpyrifos:***

The test solution containing 5-9 ml of Britton-Robinson at pH 2.0 was mixed with a suitable volume (1-5 ml) of ethanol in the polarographic cell to obtain a final aqueous volume of 10 ml. Nitrogen gas was then purged through the polarographic cell for a period of 15 mins and the polarogram of the blank was then measured out at -0.2 V starting potential vs SCE, 4 mV. sec^{-1} scan rate and 50 mV_{pp} pulse amplitude. A 0.5 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) was then added to each buffer ethanol solution in the polarographic cell and nitrogen gas was then bubbled for a period of 5 mins. The polarogram of each solution in the voltammetric cell was then recorded at the same instrumental parameters set for the corresponding background electrolyte.

2.4.1.4. ***The effect of salt on the DPP determinationof Chlorpyrifos:***

In order to investigate the salt effect on the determination of Chlorpyrifos, 5.5 ml of Britton-Robinson Buffer of pH 2.0 were mixed with 2.5 ml ethanol in a voltammetric cell. To this solution 2 ml of NaCl (0.5 M), 2 ml of $NaNO_3$ (0.5 M) or 2 ml of sodium acetate (0.5 M) were added to the voltammetric cell. The cell solution was then purged with purified nitrogen for 15 min and

the polarogram of the background electrolyte was then recorded a starting potential of E_s = -0.20 vs. SCE, 4 mV scan rate and 50 mV_{pp} pulse amplitude. Under the same experimental conditions employed a 0.5 ml of Chlorpyrifos ($1x10^{-3}$ M) was placed in the electrochemical cell and a stream of purified nitrogen gas was passed for 5 min and the polarogram was then measured.

2.4.1.5. ***Effect of sodium nitrate percentage on the DPP determination of Chlorpyrifos:***

The effect of various concentrations of sodium nitrate 0-4 ml $NaNO_3$, 0.5 M on the determination of Chlorpyrifos was critically studied. In separate experiments 3.5-7.5 ml of Britton-Robinson and 2.5 ml of ethanol were placed in the electrochemical cell. To these solutions various volumes (0.0-4 ml) of sodium nitrate were added so as to make the total volume of the solution 10 ml. The solution was then purged with dry nitrogen for 15 min and the polarogram of the background electrolyte was then measured at constant starting potential (E_s = -0.2 V vs. SCE), scan rate of 4 mV sec^{-1} and 50 mV_{pp} pulse amplitude. Under these conditions a solution 0.5 ml of $1x10^{-3}$ mol/L Chlorpyrifos was then added separately into the electrochemical cell and a stream of purified nitrogen was passed for 5 min and the polarograms were then measured separately.

2.4.1.6. *Effect of pulse amplitude on the DPP determinationof Chlorpyrifos:*

In the voltammetric cell, 7.5 ml of Britton-Robinson buffer at pH 2 were mixed with 2.5 ml of ethanol, 0.5 ml of 0.5 M sodium nitrate as a background electrolyte. Purified nitrogen was then purged through the solution cell for 15 min., the polarogram was then measured. To this solution, 0.5 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) was then placed in the electrochemical cell and a stream of purified nitrogen was passed then recorded the polarograms at various pulse amplitudes 5-100 mV and 4 mV sec^{-1} scan rate and starting potential of -0.4 V.

2.4.1.7. *Effect of scan rate on the DPP determination of Chlorpyrifos:*

In the electrochemical cell, 7.5 ml of Britton-Robinson buffer at pH 2 were mixed 2.5 ml ethanol and 0.5 ml sodium nitrate. The solution cell was then purged with purified nitrogen for 15 mins and the polarogram was then recorded at E_s = -0.4 V and 50 mV_{pp} pulse amplitude. Under the experimental conditions employed, a 0.5 ml solution of the pesticide Chlorpyrifos ($1x10^{-3}$ M) was placed in the electrochemical cell and a stream of purified nitrogen was passed for 15 min through the solution cell under stirred conditions. Measurements of DPP were then recorded at various scan rates 5, 10, 15 and 20 mV sec^{-1} separately.

2.4.1.8. ***Effect of temperature on the DPP determination of Chlorpyrifos:***

In separate experiments, 7.5 nl of Britton-Robinson buffer at pH 2 were mixed with 2.5 ml of ethanol and 0.5 ml of sodium nitrate (0.5 M) at various temperatures 25, 37, 47 and 57 °C. Each solution was then purged with dry nitrogen for about 15 min at 4 mV. sec^{-1}, starting potential of Es = -0.4 V vs. SCE and 50 mV_{pp} pulse amplitude. The polarograms of background electrolyte were then recorded at each temperature. Under the experimental conditions employed, a 0.5 ml of the Chlorpyrifos ($1x10^{-3}$ mol/L) was placed in the electrochemical cell and a stream of purified nitrogen was then passed for 5 min through the solution cell and the polarograms were then recorded at each temperature at 4 mV. sec^{-1}, -0.2 V vs. Ag/AgCl starting potential and pulse amplitude of 50 mV_{pp}.

2.4.1.9. ***Effect of concentration on the DPP determination of Chlorpyrifos:***

Exactly 7.5 ml of Britton-Robinson buffer at pH 2 was mixed with 2.5 ml of ethanol and 0.5 ml $NaNO_3$ (0.5 M) in the electrochemical cell at 25 °C. The solution was then purged with purified nitrogen for 15 mins and the polarogram of the background electrolyte was then recorded at 4 mV. sec^{-1}, 25 °C, 50 mV_{pp} pulse amplitude and starting potential -0.4 V vs. SCE. Under the experimental conditions employed different concentrations of the Chlorpyrifos pesticide ($0.99x10^{-6}$-$6.54x10^{-6}$ mol/L) were then placed in the electrochemical cell and a stream of dry nitrogen was then passed for 10 mins through the solution

cell. The polarogram at each added concentration of Chlorpyrifos under the same conditions was then recorded.

2.4.1.10. ***Influence of diverse ions on the DPP determination of Chlorpyrifos:***

The influence of diverse ions (cations and anions) which are commonly in association with the Chlorpyrifos in natural water and pesticidal formulations was critically examined. In the electrochemical cell 7.5 ml of Britton-Robinson buffer at pH 2 were mixed with 2.5 ml of ethanol and 0.5 ml $NaNO_3$. The solution was then purged with purified nitrogen for 15 min and the polarogram of the background electrolyte was then measured. A 0.5 ml of Chlorpyrifos ($1x10^{-3}$ M) was then added and purified nitrogen was then purged through the solution cell for 3 min. The polarogram was then recorded at the same experimental conditions of background electrolyte of Es = -0.4 V, 4 mV. sec^{-1} and 25 °C. Under the employed experimental conditions in the presence of a 0.5 ml solution of Chlorpyrifos ($1x10^{-3}$ M) was then placed in the electrochemical cell and exactly 0.5 ml of 0.5 mol/L metal ion ((Ca^{2+}, Mg^{2+}, Cd(II), Zn(II), Cu(II), Cr (VI)) or 0.5 mol/L of various anions (NO_3^-, F^-, I^-, SO_4^{-2}, Cl^-, Cr_2O^{-2} were added separately to the electrochemical cell and a stream of purified nitrogen was passed through the cell for 3 min. Measurements of the polarogram of each solution was then carried out separately at the same optimum experimental conditions of the background plus the tested pesticide.

2.4.1.11. *Application of DPP in the determination of Chlorpyrifos:*

A) Analysis of Chlorpyrifos in distilled and tap water:

In the polarographic cell, mix 7 ml of Britton-Robinson buffer (pH 2) with 2.5 ml absolute ethanol and 0.5 ml of sodium nitrate (0.5 M). The solution was then purged with purified nitrogen gas for 15 mins and the polarogram of the background electrolyte was then recorded at -0.4 V vs. SCE, 4 mV sec^{-1} scan rate and 50 mVpp pulse amplitude. This solution was then spiked with different volumes (1- 5 ml) of commercial Chlorpyrifos (0.026 gl^{-1} dissolved in distilled or tap-water) or pure Chlorpyrifos (0.01 gl^{-1} dissolved in water - ethanol mixture (10%, v/v) and the solution was then purged with purified nitrogen for 5 mins. The polarograms were then recorded under the same experimental conditions of background electrolyte.

B) Analysis of Chlorpyrifos in underground water:

A 7 ml of Britton-Robinson buffer was mixed with 2.5 ml of absolute ethanol and 0.5 ml of sodium nitrate in the polarographic cell. The cell solution was then purged with purified nitrogen for 15 min under stirred conditions. The voltammogram of the background electrolyte was then measured at a starting potential of -0.4 V vs. SCE, 4 mV. sec^{-1} scan rate and 50 mV_{pp} pulse amplitude. To this solution various volumes (1-5 ml) of commercial (0.24 gl^{-1}) or pure Chlorpyrifos (0.01 gl^{-1}) in ethanol - underground water system (1:10 v/v) were then added and the solution was purged with purified nitrogen for 5 mins under stirred conditions. The voltammograms were then recorded at each addition of Chlorpyrifos and the concentration

of the Chlorpyrifos was then determined from standard curve constructed under the same experimental conditions of background electrolyte and the tested analyte.

2.4.2. Differential pulse cathodic adsorptive stripping voltammetric (DP-CASV) determination of Chlorpyrifos:

2.4.2.1. *Influence of pH on DP-CASV determination of Chorpyrifos:*

In the voltammetric cell, mix 7.5 ml of Britton-Robinson buffer at various pH (2-11) with 2.5 ml of ethanol and 0.5 ml of sodium nitrate (0.5 M) and then pass the purified nitrogen through the electrochemical cell for 16 min under stirred conditions. Record the differential pulse-adsorptive cathodic voltammetry of the background electrolyte at an accumulation potential of -0.2 V vs. Ag/AgCl, deposition time of 60 s, 10 mV. sec^{-1} scan rate and pulse amplitude of 50 mV_{pp}. Under the experimental conditions employed a solution of 0.01–0.05 ml of the Chlorpyrifos ($1x10^{-3}$ mol/L) was added and a stream of purified nitrogen was passed for 3 min through the solution cell under stirred conditions.

2.4.2.2. *Influence of sodium nitrate percentage on the DP-CASV determination of Chlorpyrifos:*

In separate experiments different volumes (4.5-7 ml) of Britton-Robinson buffer were mixed with 2.5 ml of ethanol and various amounts (0.5-3 ml) of sodium nitrate (0.5 M) in the electrochemical cell. The solution in the electrochemical cell was then purged with purified nitrogen for 16 min and the background voltammogram of each solution at accumulation

potential of -0.2 V vs. Ag/AgCl, deposition time 120 sec, 10 mV. sec^{-1} scan rate and 50 mV_{pp} pulse amplitude. Under the same experimental conditions employed a solution of 0.5 ml of Chlorpyrifos ($1x10^{-4}$ mol/L) was then placed in the electrochemical cell and a stream of purified nitrogen was passed through the electrochemical cell under stirred conditions. The voltammograms of the solutions were then measured at accumulation potential of -0.2 V vs. AgCl, accumulation time of 120 sec, pulse amplitude of 50 mV_{pp} and 10 mV. sec^{-1} scan rate.

2.4.2.3. ***Influence of ethanol concentration on DP-CASV determination of Chlorpyrifos:***

In separate experiments different volumes (6-8 ml) of Britton-Robinson buffer at pH 2 were mixed with 1 ml sodium nitrate (0.5 M) and various amounts (1-3 ml) of pure ethanol. The solution in the electrochemical cell was then purged with purified nitrogen for 16 min and the voltammograms of the background electrolyte were then measured at accumulation potential of -0.2 V vs. Ag/AgCl, deposition time of 120 sec, pulse amplitude of 50 mV_{pp} and 10 mV. sec^{-1} scan rate. The same experimental conditions were then employed after adding 0.05 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) and passing purified nitrogen for 3 min through the electrochemical cell. Record the voltammograms of the final solution.

2.4.2.4. *Influence of scan rate and pulse amplitude on DP-CASV determination of Chlorpyrifos:*

In the electrochemical cell 7 ml of Britton-Robinson buffer at pH 2 were mixed with 2 ml of ethanol and 1 ml of sodium nitrate (0.5 M). The solutions was then purged with purified nitrogen for 15 min under stirred conditions. The voltammogram of the background electrolyte was then recorded at various scan rate (2–20 mV. sec^{-1}) and pulse amplitude (5–100 mV). Following the same experimental conditions, a solution of 0.05 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) was then introduced in the electrochemical cell and a stream of purified nitrogen was then passed for 3 min under stirred conditions. Record the voltammogram of the solution at the same scan rate, pulse amplitude, accumulation potential time of -0.2 V vs. Ag/AgCl and deposition time of 120 sec. .

2.4.2.5. *Influence of accumulation potential on the DP-CASV determination of Chlorpyrifos:*

In the electrochemical cell mix 7 ml of Britton-Robinson buffer at pH 2 with 2 ml of ethanol and 1 ml of sodium nitrate (0.5 M). Percolate purified nitrogen through the electrochemical cell for 16 min under stirred conditions. Record the voltammograms of the background electrolyte at 120 sec deposition time and various accumulation potential (-0.2--0.8 V) vs. Ag/AgCl. Under the same experimental conditions employed, a solution of 0.05 ml of Chlorpyrifos ($1x10^{-3}$ mol/L) was placed in the electrochemical cell and a stream of purified nitrogen was then passed through the

cell for 3 min under stirred conditions. Record the voltammograms at 120 sec, pulse amplitude of 50 mV, 5 $mV.sec^{-1}$ scan rate at various accumulation potential.

2.4.2.6. ***Influence of deposition time on the DP-CASV determination of Chlorpyrifos:***

Under the previous optimum experimental conditions of pulse amplitude, scan rate and accumulation potential mix 7 ml of Britton-Robinson buffer at pH 2 with 2 ml ethanol and 1 ml sodium nitrate in the voltammetric cell. Purified nitrogen gas was then purged through the solution cell for 3 min under stirred conditions. Record the voltammogram of the background electrolyte at various deposition time (0-180 sec^{-1}) at the optimum scan rate and accumulation time. Repeat the same experimental after placing 0.05 ml of Chlorpyrifos in the electrochemical cell and passing a stream of purified nitrogen for 10 min through the cell under stirred conditions. Record the voltammogram of the solution at each deposition time.

2.4.2.7. ***Influence of diverse ions on the DP-ACSV determination of Chlorpyrifos:***

The interference of various ions, e.g. copper(II), lead(II), chromium(III), chromium(VI) and zinc(II), ions at a 25:1 (interferent: analyte) approximately exceeding those normally found in natural water was critically investigated on the DP-CASV determination of Chlorpyrifos. In the voltammetric cell 7 ml of Britton-Robinson buffer at pH 2 were mixed with 2 ml of ethanol and 1 ml of sodium nitrate (0.5 M). To this solution

exactly add 0.05 ml of Chlorpyrifos ($1x10^{-3}$ M) and record the voltammogram after purging purified nitrogen for 10 min under stirred conditions at the optimum conditions of deposition time, pulse amplitude, accumulation and potential scan rate. Repeat the same experimental conditions in the presence of each of the added metal ion separately and record the voltammograms.

2.4.2.8. ***Application of DP-CASV in the determination of Chlorpyrifos:***

A) Analysis of Chlorpyrifos in the commercial formulations, tap and underground water:

In the voltammetric cell, 7 ml of Britton-robinson buffer of pH 2 were mixed with 2 ml of absolute ethanol and 1 ml of nitrate solution (0.5 M). The cell solution was then purged with dry nitrogen for 16 mins under stirred conditions and the voltammogram of the background electrolyte was then measured at -0.4 V vs. Ag/AgCl, deposition time of 120 sec, 5 mV. sec^{-1} scan rate and 50 mVpp pulse amplitude. To this solution, various volumes (0.5-5 ml) of commercial Chlorpyrifos (0.025 gl^{-1} in distilled water) were spiked into the electrochemical cell. The solution was then purged with dry nitrogen and the voltammogram for each solution was then measured under the same experimental conditions of the background electrolyte. The final pesticide concentration was then obtained with the aid of standard curves. Employing the same experimental procedures, analysis of various volumes (1-5 ml) of spiked Chlorpyrifos (0.025 gl^{-1}) in tap-, underground- and treated waste water were critically carried out and the final pesticide concentration was

then determined with the aid of concurrent calibration curve made under the same experimental conditions.

B) Detection and semiquantitative determination of Chlorpyrifos in tomato plants:

A 1-kg amount of air-dried ground sample of tomato plant treated with Chlorpyrifos for different times (0-120 hrs) was accurately weighed into porcelain basin. The grounded sample was then soaked and rinsed four times with 50 ml of n-hexane for about 1 hr. The n-hexane extract was then evaporated with a rotary evaporator and the solid residue was then dissolved with 10 ml ethanol and the solution was then coupled to 25 ml with distilled water in measuring flask. Various volumes (1-5 ml) of this solution were then added to an electrochemical cell containing 7 ml of Britton-Robinson buffer at pH 5.01 ml of ethanol and 1 ml of sodium nitrate (0.5 M). The solution cell was then purged with dry nitrogen for 15 mins under stirred conditions and the voltammogram was then recorded at -0.4 V vs. Ag/AgCl, deposition time of 240 sec. 5 mV. sec^{-1} scan rate and 50 mV_{pp} pulse amplitude. The detection of the Chlorpyrifos was made by observing the cathodic peak found at -1.2 V vs. Ag/AgCl. The semiquantitative determination of the pesticide was also made by comparison peak height current at -1.2 V in the voltammogram with a calibration curve made with Chlorpyrifos in distilled water. Moreover, determination of Chlorpyrifos pesticide was carried out using standard addition method.

Results and Discussion

CHAPTER III

"Differential Pulse Polarographic Determination of Chlorpyrifos"

3.1. Differential Pulse Polarographic Determination of Chlorpyrifos

Polarography involves the electrochemical analysis of solution containing oxidizable and/or reducible species. The analysis is carried out in a three electrodes electrochemical cell containing a dropping mercury electrode (DME) as a working electrode. The DME consists of a fine capillary through which mercury passes and the mercury drops are formed at a rate of about one every few seconds. The potential of the DME is changed linearly with time relative to a reference saturated calomel electrode (SCE). Once the potential is reached to the value at which a species in solution can react, current flows between the DME and third "counter" Pt-electrode.

To understand how both quantitative and qualitative information about the species in solution could be obtained by polarography, it is necessary to consider the processes occurring at the DME. Ions or molecules approach and depart from the working electrode surface under the influence of the electrostatic attraction (migration) and diffusion processes. Migration phenomena is a process involving movement of the ions or molecules which take place under the influence of an electric field, on the other hand the diffusion processes is the motion of the species which is mainly dependent on the concentration gradient of the species and is not affected by the DME potential or by the charge of the species in the tested solution. In polarography, the solution conditions are adjusted to eliminate migration so that all ions or molecules reach at the

electrode surface do so only through diffusion process. Hence, in polarography, diffusion-controlled currents, which are proportional to the concentration of the species under investigation, are measured. Over the last number of years, various polarographic methods have been developed and successfully employed in the area of environmental analysis. However, differential pulse polarography (DPP) is the most widely used because of its sensitivity and reproducibility. On the other hand, the applicability of the polarographic methods in the area of biological and pesticide analysis is limited by overlapping with catalytic hydrogen discharge and the possible adsorption of depolarizer on the mercury surface. Normal and differential pulse polarography have been used to overcome these problems (Nurnberge, 1960).

The differential pulse polarographic technique gains greater sensitivity by taking the advantage of the fact that a small jump in potential (A superimposed small potential pulse ca 50 mv is applied on the top of the DC-potential ramp near the end of the life time of each mercury drop) has a much greater effect on the analytical signal than on source of noise such as capacitive current. A differential technique based on a small potential pulse minimizes the signal/noise ratio leading to greater sensitivity. Therefore, the limit of detection of organic and inorganic analysis using DPP are in the range 10^{-7}-10^{-6} mol/l, which for the classical DC polarography it would be only about 0.5×10^{-4} mol/l.

Fig. 3.1 shows the differential pulse polarographic peak of $5x10^{-5}$ mol/l of CP at pH 3.2 in solution containing 25% (v/v) ethanol. This peak results from applying waveform which has pulse of constant amplitude superimposed on a negative going ramp. The DPP peak is probably corresponding to the cathodic reduction wave of the azomethine centre ($\diagdown C = N \diagup$) of the pyridine ring. According to the well-known reduction mechanism of the N-heterocyclic compounds the $\diagdown C = N \diagup$ undergoes in acid to neutral media a totally irreversible electrode reaction with a total uptake of 2-electrons and 2-protons ($2e^-/2H^+$) (Kamal, 1991). It should be mentioned that the N-heterocyclic compounds are characterized by a well resolved cathodic reduction peak located at more negative potential, close to hydrogen ions discharge potential. This behaviour could be explained by: (i) the one pair of electrons at the nitrogen atom cause the reduction process to be more difficult and (ii) the catalytic effect of the N-heterocyclic compounds (Scheme I) on the H^+ discharge shifts the background discharge to less negative potential as follows:

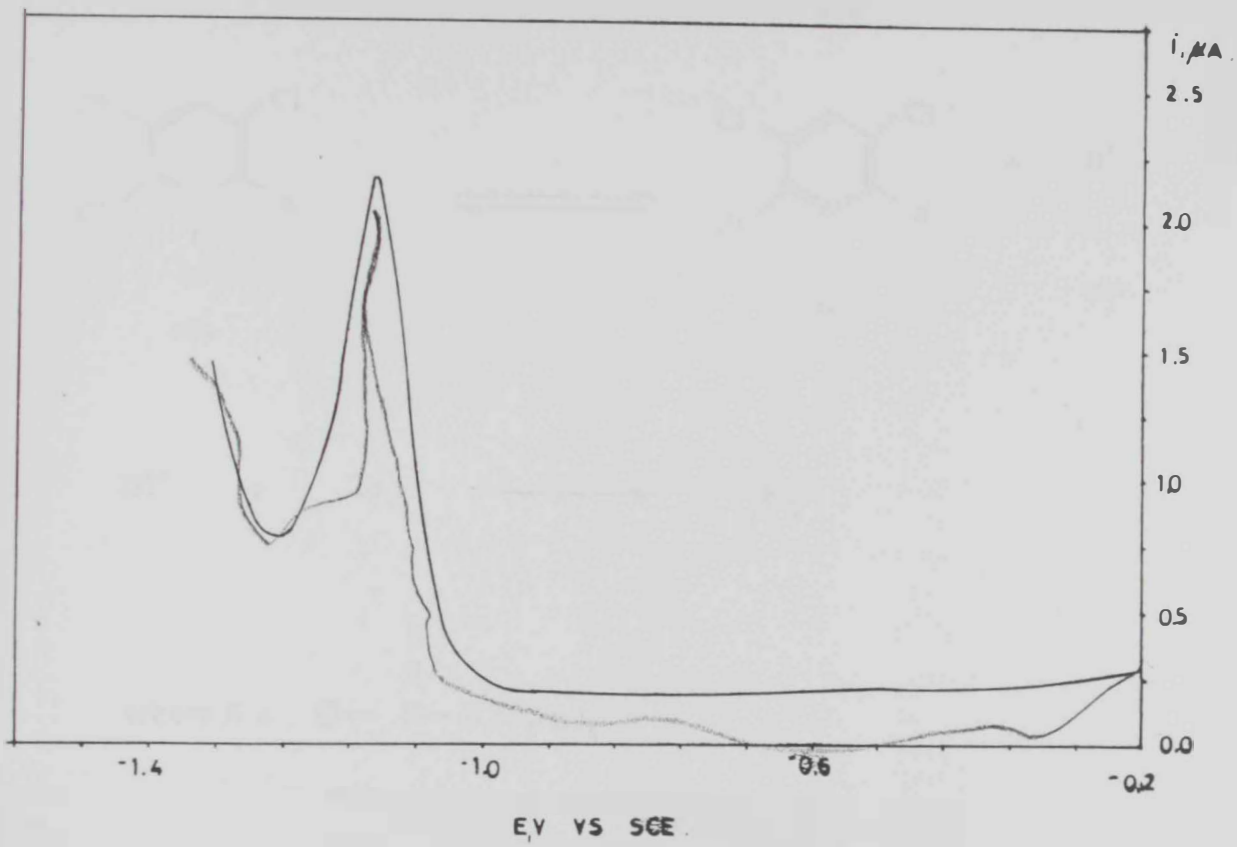
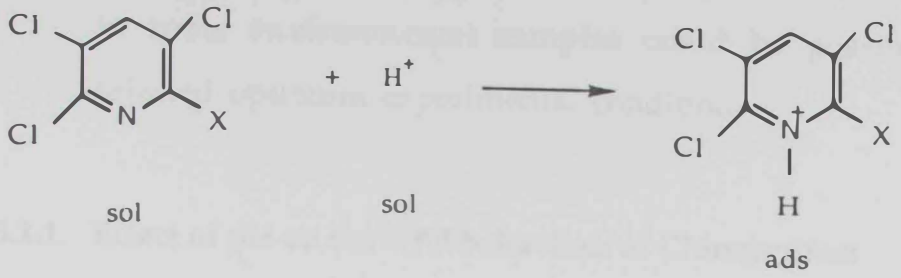
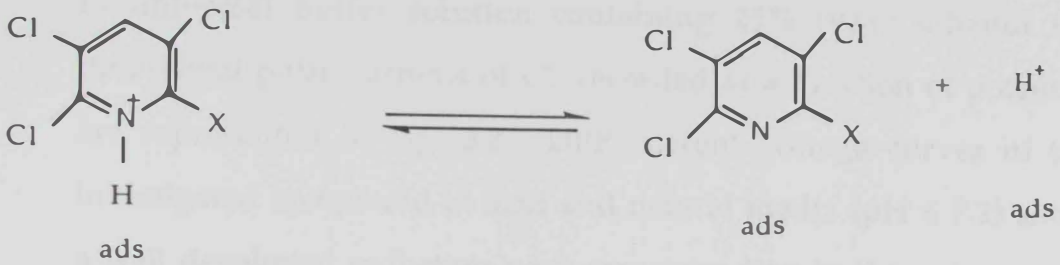


Fig. 3.1. : DPP behaviour of 5×10^{-5} mol/L of CP at pH 3.2 in solution containing 25% ethanol. Pulse amplitude 50 mV, drop time 1.4 s and scan rate 2 mV/s.



(1)



(2)

$$2H^+ + 2e \longrightarrow H_2 \qquad (3)$$

where X = $O-\overset{\overset{S}{\|}}{P}-(OC_2H_5)_2$

Scheme I

The determination of a compound characterized with a DPP peak very close to the background discharge is difficult. Therefore, we will try to select the operational and solution conditions which give a well resolved cathodic reduction peak from the background discharge as well as which gave the most sensitive DPP peak. Under the optimum operating conditions (pulse amplitude, scan rate and drop time) and solution conditions (pH, ionic strength, nature of supporting electrolyte and percentage of ethanol) we expect that the CP can be determined to very low concentrations.

Also, the application of the DPP technique for determination of CP in some environmental samples could be possible under the selected optimum experimental conditions.

3.1.1. Effect of pH on the DPP behaviour of Chlorpyrifos:

In universal buffer solution containing 25% (v/v) ethanol the differential pulse currents of CP recorded as a function of potential are represented in Fig. 3.2. DPP current voltage curves of the investigated compound in acid and neutral media (pH ≤ 7.2) show a well developed reduction peak corresponding to the reduction of $\diagdown\!\!\diagup C = N$ centre of the pyridine ring via $2e^-/2H^+$ mechanisms (Scheme II). Under various conditions the pyridine moiety was found polarographically inactive. However, in the investigated compound (CP) the mesomeric effect of the three chlorine atoms attached to the pyridine moiety increases the localization of the electrons in the pyridine system and consequently enhance the reducibility of the $\diagdown\!\!\diagup C = N$ centre.

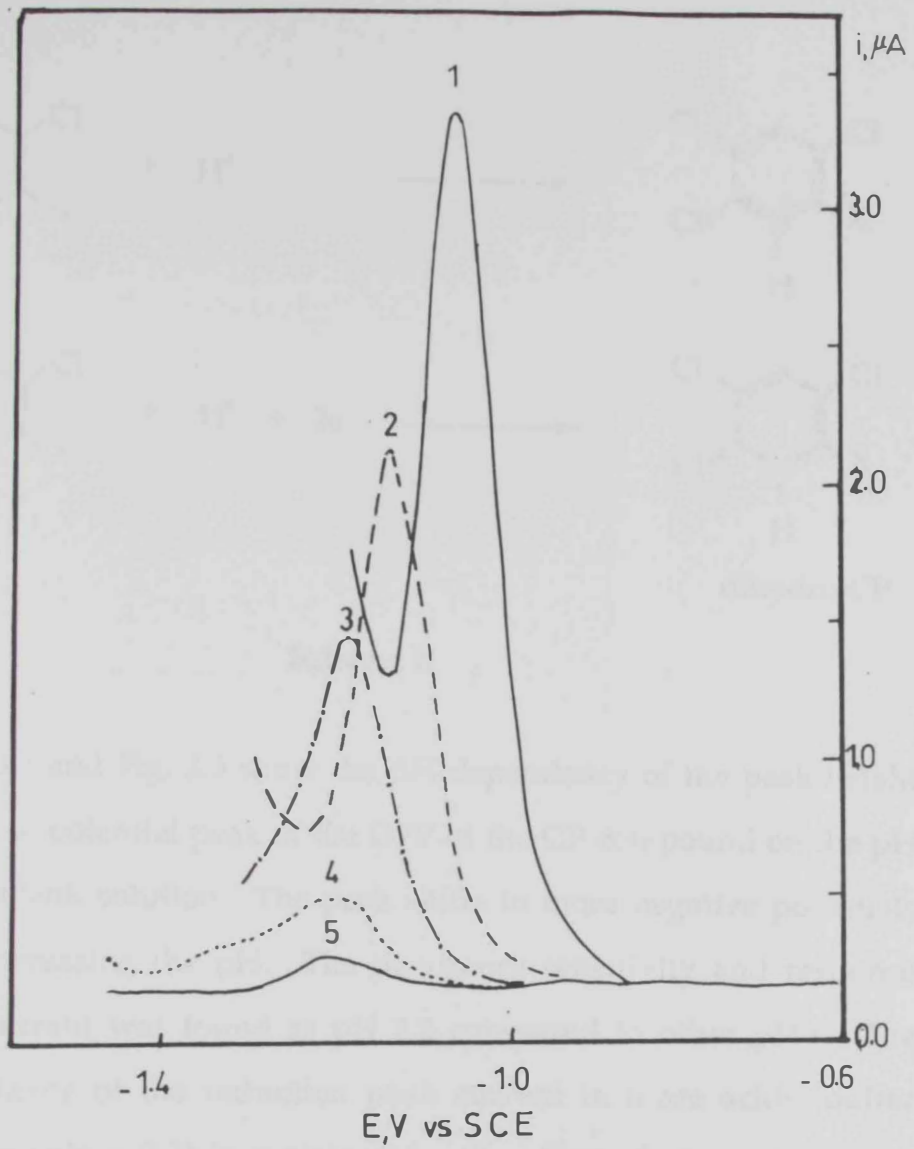
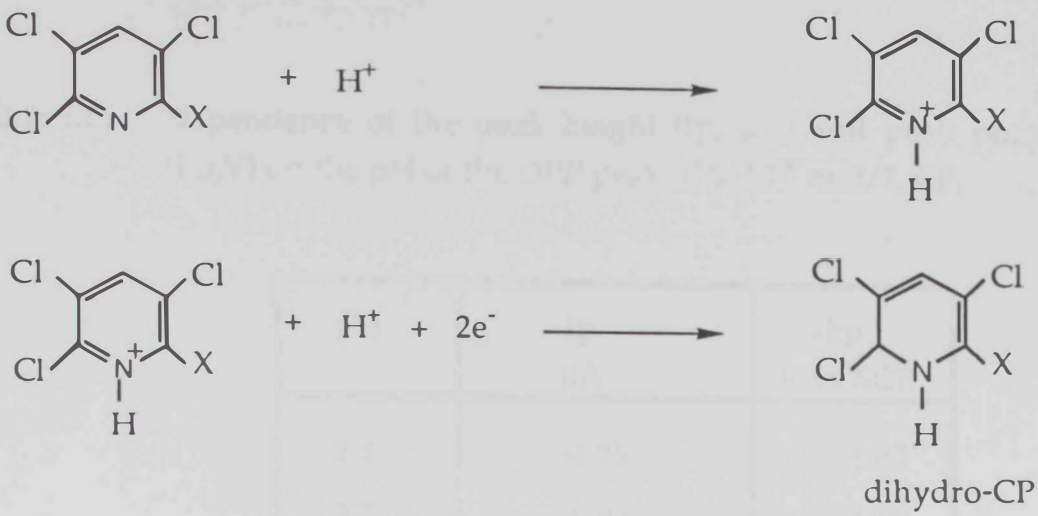


Fig. 3.2. : Effect of pH on the DPP behaviour of 5×10^{-5} M CP, (1) pH 2.2, (2) 3.2, (3) 4.0, (4) 7.2 and (5) pH 9.0. Other conditions as in Fig. 3.1.



Scheme II

Table 3.1 and Fig. 3.3 show the pH dependency of the peak height and peak potential peak of the DPP of the CP compound on the pH of the blank solution. The peak shifts to more negative potentials with increasing the pH. The maximum sensitivity and response peak current was found at pH 2.2 compared to other pH's. The inconstancy of the reduction peak current in more acidic buffer solution (pH < 2.2) is explained by the effect of strong hydrogen evolution and the peak is completely overlapped with the background discharge. As the pH approaches the moderately acidic and nuetral range the reduction response decreases analogously to an acid dissociation curve (Fig. 3.3) because the protonation kinetics under these circumstances contribute progressively to the control of the overall rate of the reduction (Temerk and Kamal, 1981). Therefore, it can be concluded that pH 2.2 is the optimum pH for the determination of the investigated compound using DPP at the DME.

Table 3.1 : Dependence of the peak height (ip, μA) and peak potential (Ep,V) on the pH of the DPP peak of $5x10^{-5}$ mol/L CP.

pH	ip μA	-Ep V vs SCE
2.2	31.25	1.05
3.2	19.00	1.12
4.0	12.75	1.18
5.01	3.37	1.20
7.2	1.12	1.20
9.0	1.00	1.20

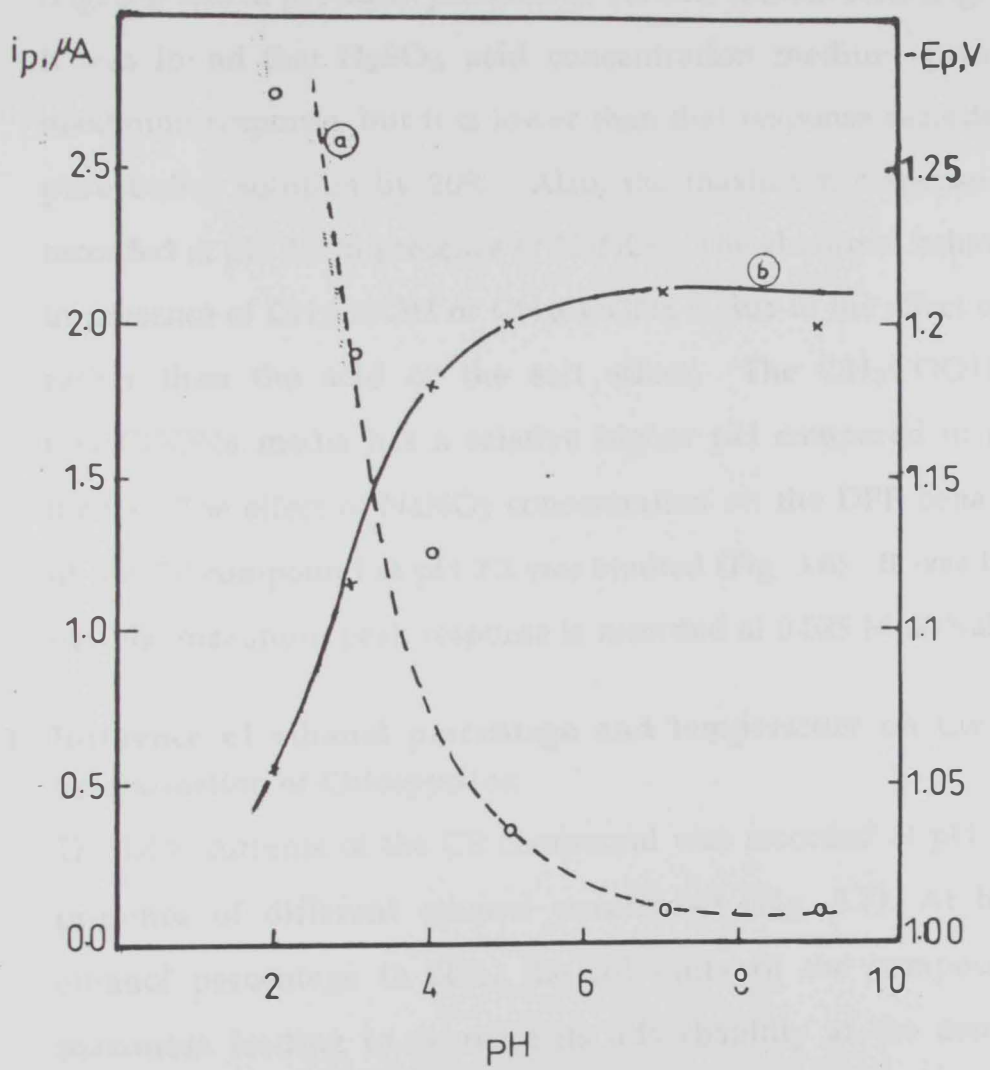


Fig. 3.3. : i_p-pH (a) and Ep-pH (b) plot of the DPP peak of 5×10^{-5} mol/L CP.

3.1.2. Influence of the nature of the supporting electrolyte, acid and salts concentration on the DPP determination of Chlorpyrifos:

In order to investigate the effect of the nature of the supporting electrolyte solution on the DPP response of the CP compound, the DPP behaviour was recorded at pH 2.2 in unbuffered acid solutions (Fig. 3.4) and at pH 2.2 in presence of various sodium salts (Fig. 3.5). It was found that H_2SO_4 acid concentration medium gave the maximum response, but it is lower than that response recorded in pure buffer solution by 20%. Also, the maximum response was recorded at pH 2.2 in presence of $NaNO_3$. The abnormal behaviour in presence of CH_3COOH or CH_3COONa is due to the effect of pH rather than the acid or the salt effect. The CH_3COOH or CH_3COONa media has a relative higher pH compared to other media. The effect of $NaNO_3$ concentration on the DPP behaviour of the CP compound at pH 2.2 was studied (Fig. 3.6). It was found that the maximum peak response is recorded at 0.025 M of $NaNO_3$.

3.1.3. Influence of ethanol percentage and temperature on the DPP determination of Chlorpyrifos:

The DPP currents of the CP compound was recorded at pH 2.2 in presence of different ethanol percentage (Fig. 3.7). At higher ethanol percentage ($\geq$ 30%) the solubility of the compound is maximum leading to decrease its adsorbability at the dropping mercury electrode surface and consequently its reduction efficiency was decreased. However, at lower ethanol percentage ($\leq$ 5%) the solubility of CP decreases and the solution in the polarographic cell becomes turbid. Thus, the maximum peak height of the DPP peak of the investigated compound was found at 25 % (v/v) of ethanol.

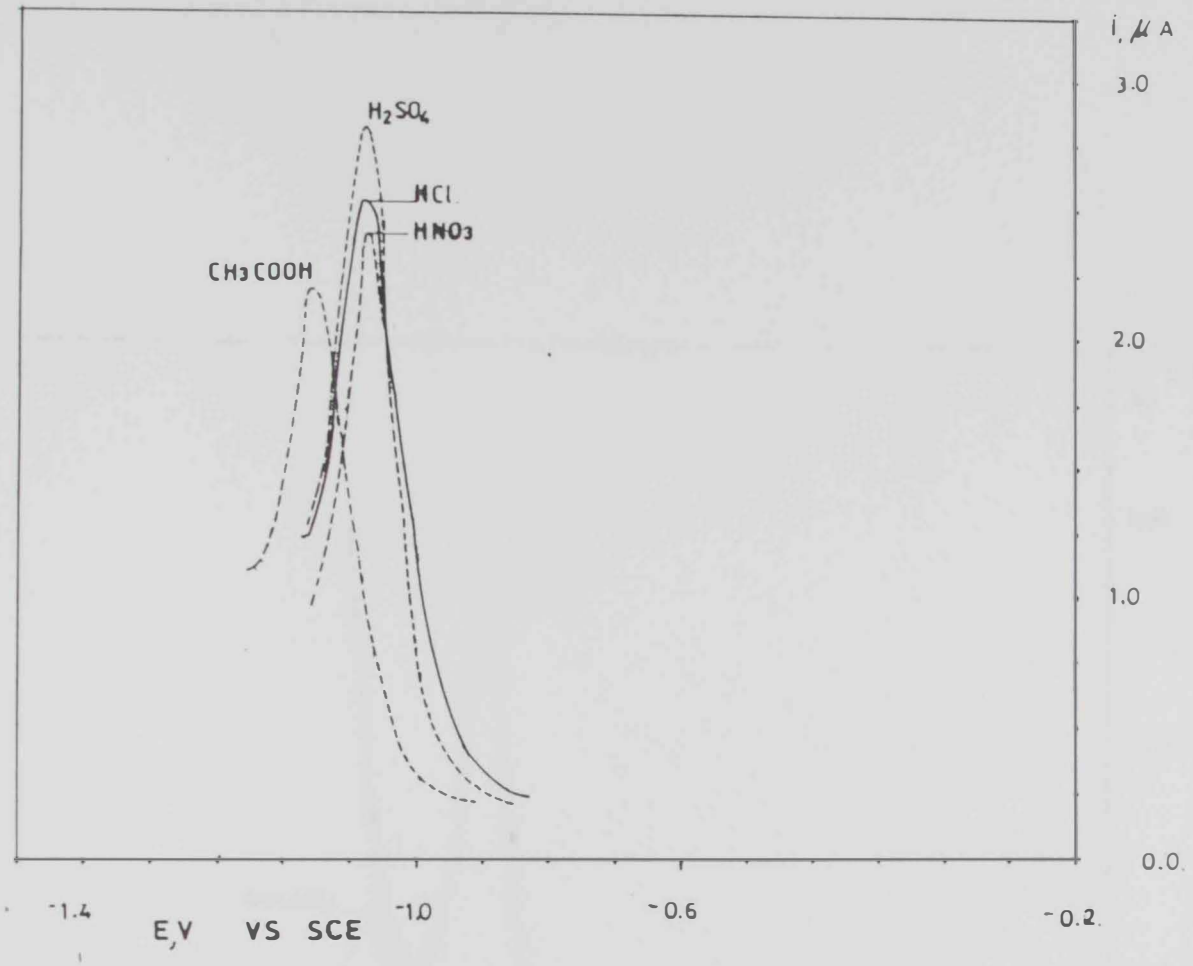


Fig. 3.4. : DPP behaviour of 5×10^{-5} mol/L Cp in unbuffered acid solutions (1×10^{-2} mol/L acid, pH 2.2).

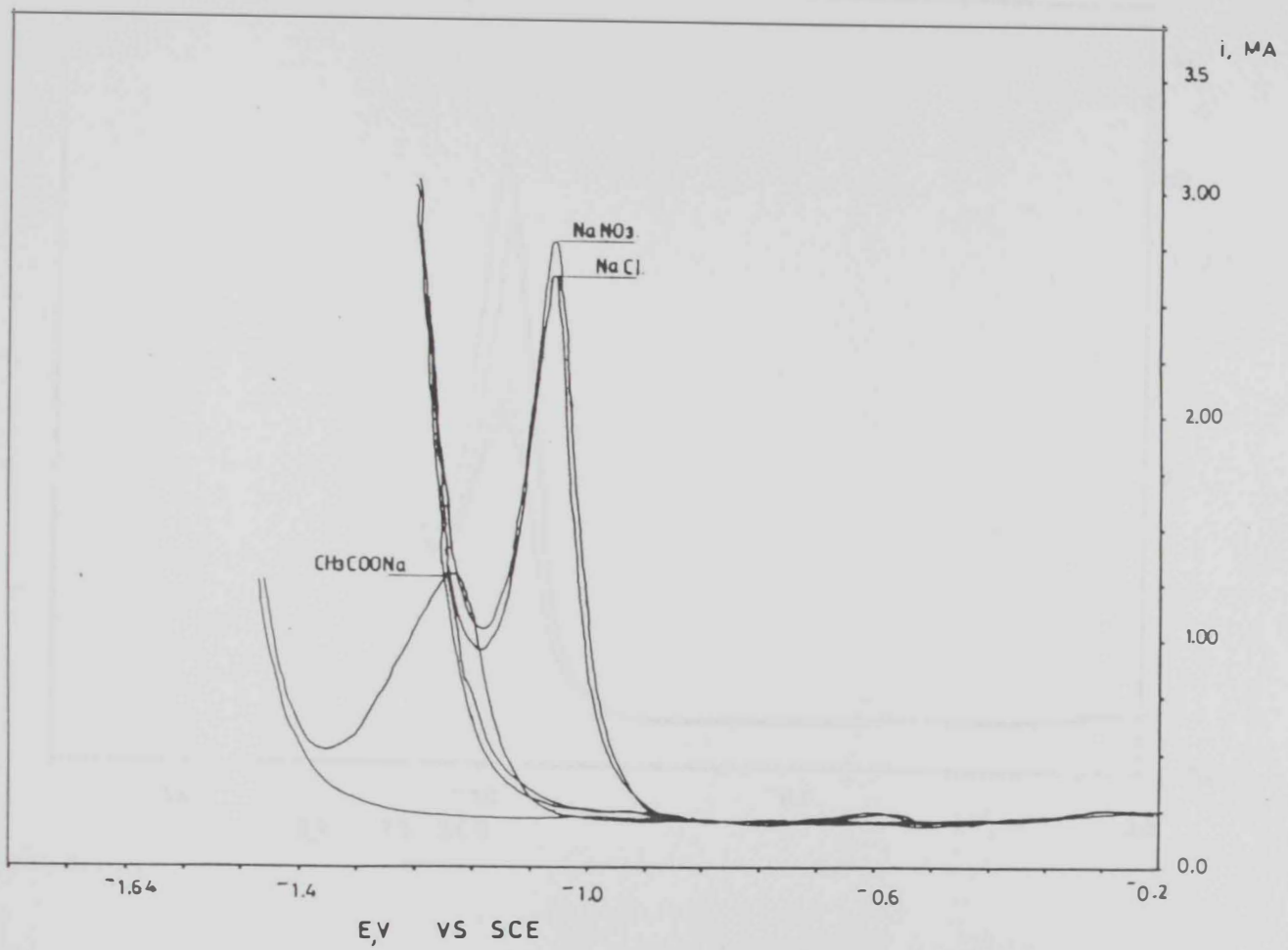


Fig. 3.5. : DPP behaviour of $5x10^{-5}$ mol/L CP at pH 2.2 in presence of 0.05 mol/L sodium salts.

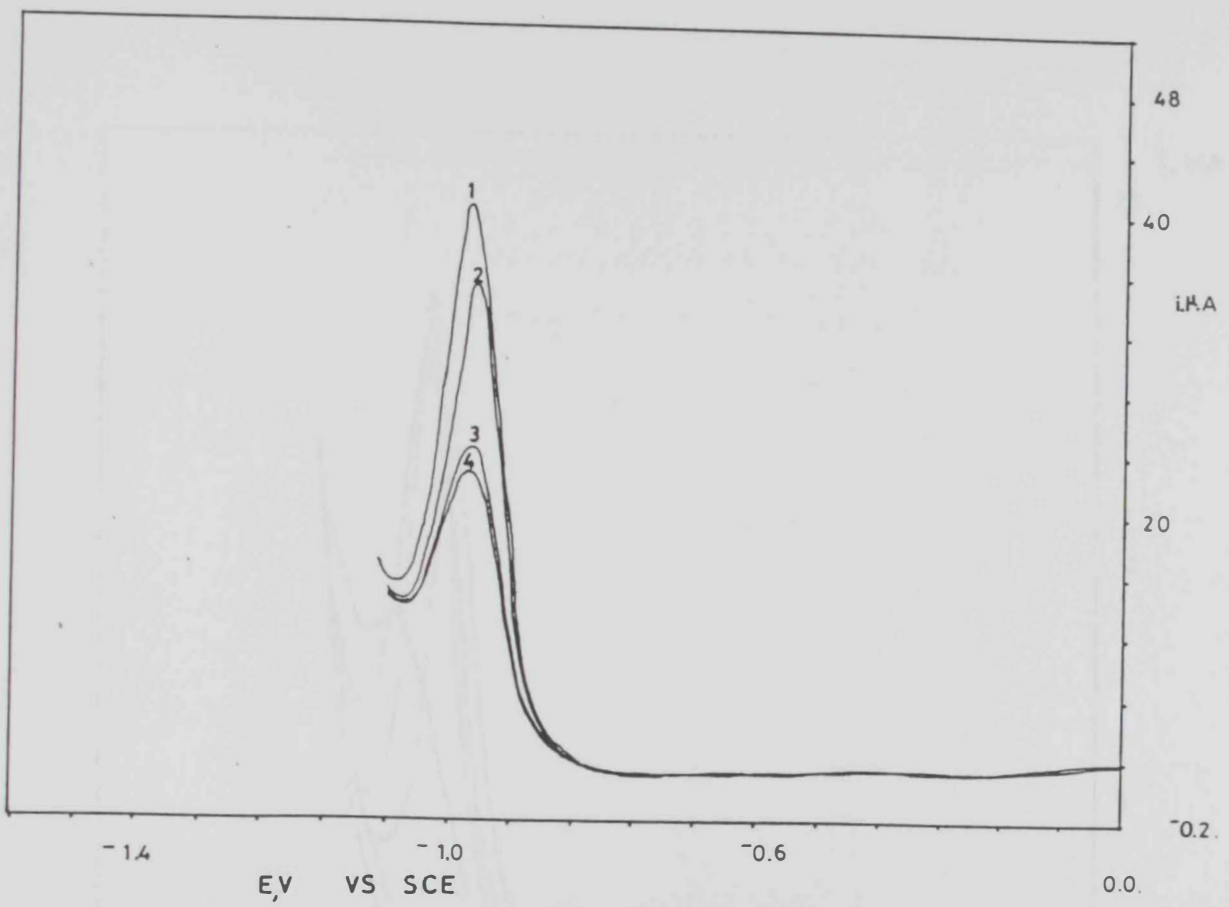


Fig. 3.6. : DPP behaviour of $5x10^{-5}$ mol/L CP at pH 2.2 in presence of (1) ≤ 0.025, (2) 0.05, (3) 0.075 and (4) 0.1 mol/L $NaNO_3$.

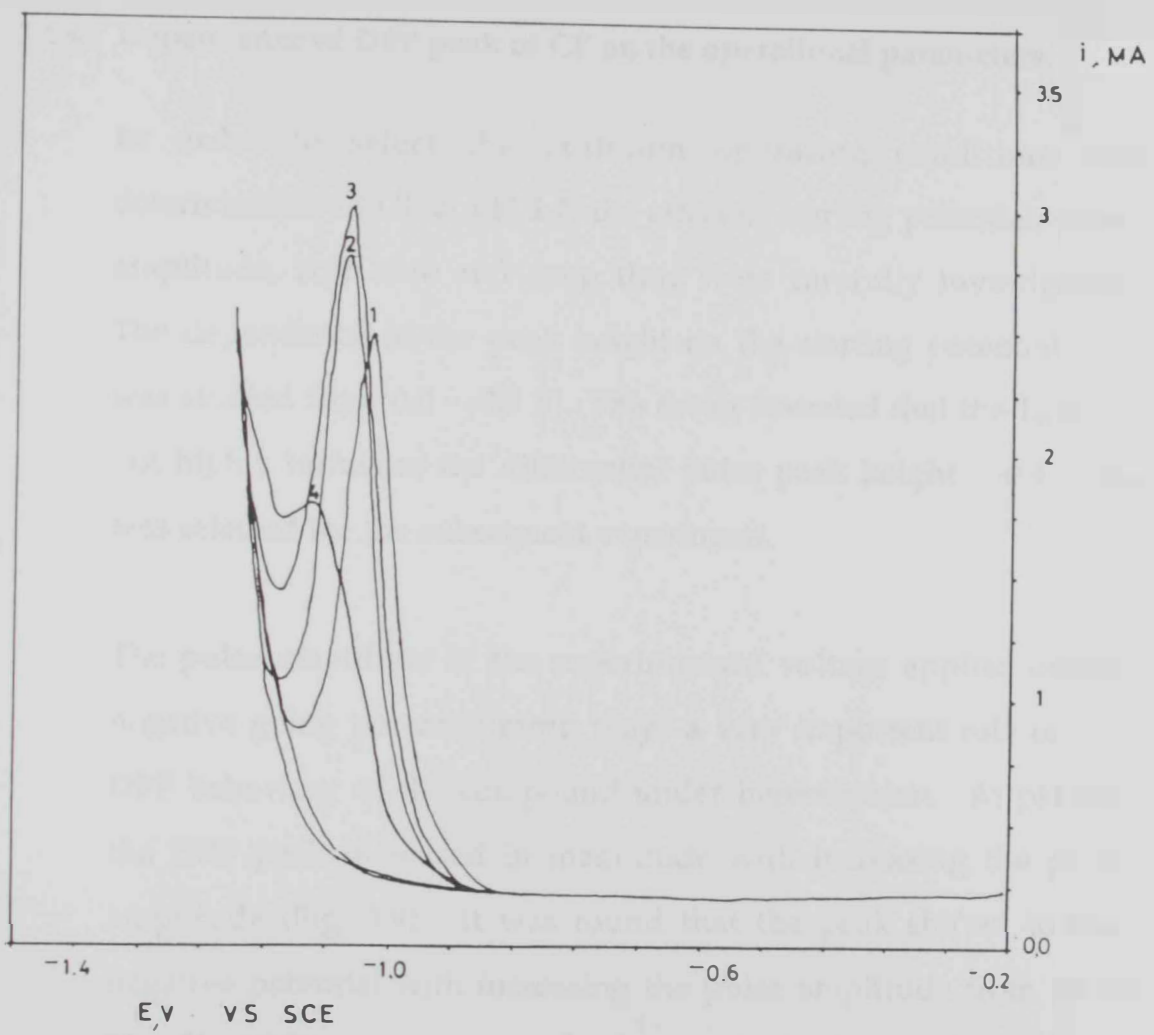


Fig. 3.7. : DPP behaviour of $5x10^{-5}$ mol/L CP at pH 2.2 in presence of different ethanol percentages. (1) 10, (2) 20, (3) 25 and (4) 30% ethanol.

The effect of temperature on the differential pulse peak height of the investigated compound was critically carried out over 25-57 °C temperature range (Fig. 3.8). The result indicated that the temperature does not highly influences the differential pulse currents of the reduction peak of the CP compound. Therefore, all subsequent experiments were carried out at room temperature.

3.1.4. Dependence of DPP peak of CP on the operational parameters:

In order to select the optimum operating conditions for determination of CP at pH 2.2, the effect of starting potential, pulse amplitude, scan rate and drop time were carefully investigated. The dependency of the peak height on the starting potential (E_s) was studied from 0.0 - -0.8 V. The result revealed that the E_s does not highly influence the differential pulse peak height. -0.4 V E_s was selected for the subsequent experiment.

The pulse amplitude of the superimposed voltage applied on the negative going potential ramp plays a very important role on the DPP behaviour of the compound under investigation. At pH 2.2, the DPP peak increased in magnitude with increasing the pulse amplitude (Fig. 3.9). It was found that the peak shifted to less negative potential with increasing the pulse amplitude from 20 to 50 mV and becomes well resolved from the background discharge. The DPP determination of CP compound was carried out at 50 mV pulse amplitude.

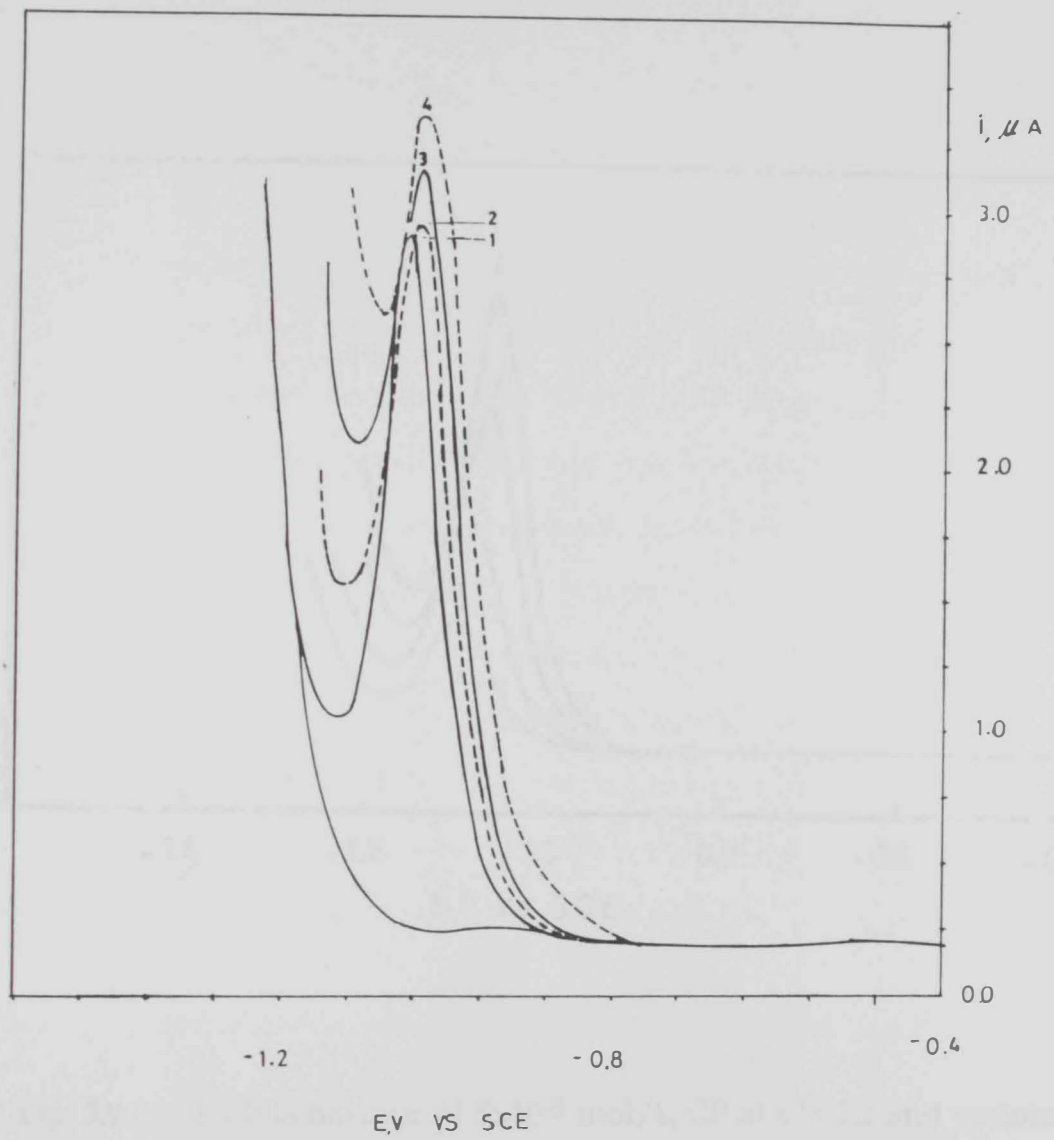


Fig. 3.8. : Effect of temperature on the DPP peak of 5×10^{-5} mol/L CP at pH 2.2. (1) 25, (2) 37, (3) 47 and (4) 55 °C.

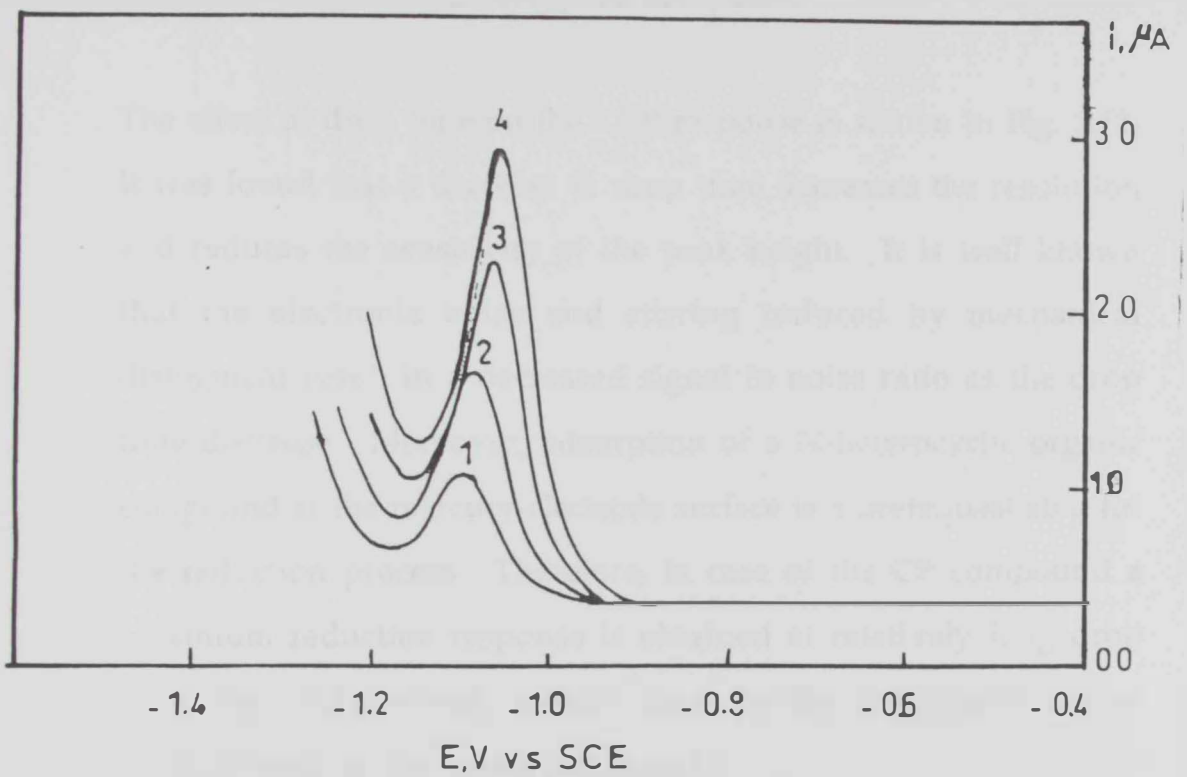


Fig. 3.9. : DPP behaviour of $5x10^{-5}$ mol/L CP at pH 2.2 and various pulse amplitudes. (1) 20, (2) 30, (3) 40 and (4) 50 mV.

The scan rate dependency of the DPP peak of $5x10^{-5}$ mol/l of CP was studied at pH 2.2 over 2-20 mV/s scan rate (Fig. 3.10). At relatively higher scan rate (scan rate > 8 mV/s) the peak height of DPP peak decreased markedly by ca 10%. The response of the cathodic reduction peak at 2 mV/s was very similar to that at 4 mV/s. Therefore, 4 mV. sec^{-1} scan rate was selected for the determination of the investigated compound.

The effect of drop time on the DPP response is shown in Fig. 3.11. It was found that a decrease in drop time decreases the resolution and reduces the sensitivity of the peak height. It is well known that the electronic noise and stirring induced by mechanical dislogment result in a decreased signal to noise ratio as the drop time decrease. Moreover, adsorption of a N-heterocyclic organic compound at the mercury electrode surface is a prerequest step for the reduction process. Therefore, in case of the CP compound a maximum reduction response is obtained at relatively long drop time e.g., 1.4 second, which used in the calibration curve measurement of the tested compound.

3.1.5. Quantitative determination of Chlorpyrifos pesticide by DPP:

The optimum conditions for the analytical determination of the investigated compound by DPP were found at pH 2.2 in the presence of (0.025 M) $NaNO_3$ and 25% (v/v) ethanol, 25 °C, 50 mV pulse amplitude, 2 mV sec^{-1} scan rate and drop time 1.4 s. Fig. 3.12 shows the DP polarograms of various concentrations

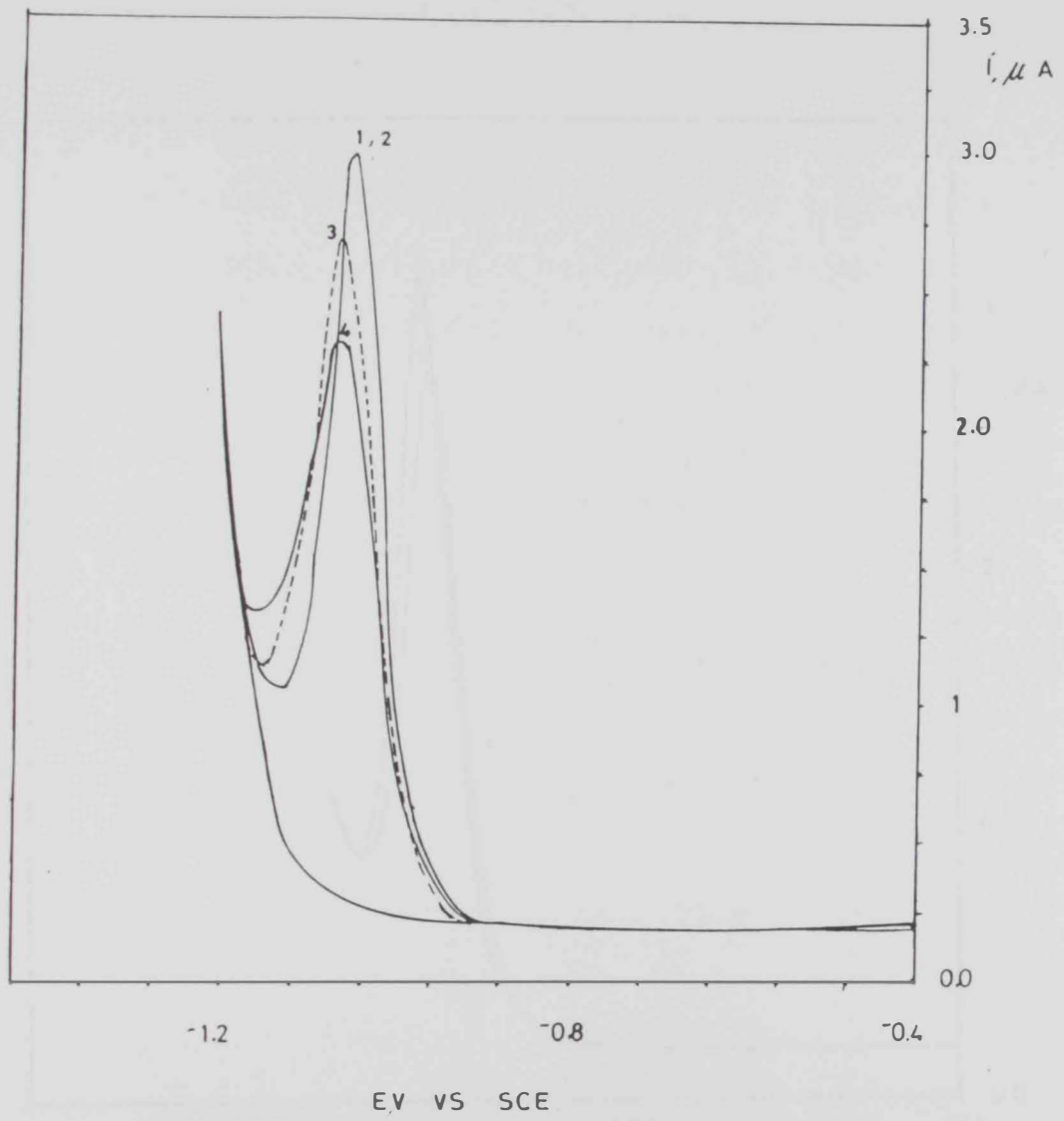


Fig. 3.10. : The DPP behaviour of $5x10^{-5}$ mol/L CP at pH 2.2 and different scan rates. (1) 2, (2) 4, (3) 10 and (4) 20 mV/s.

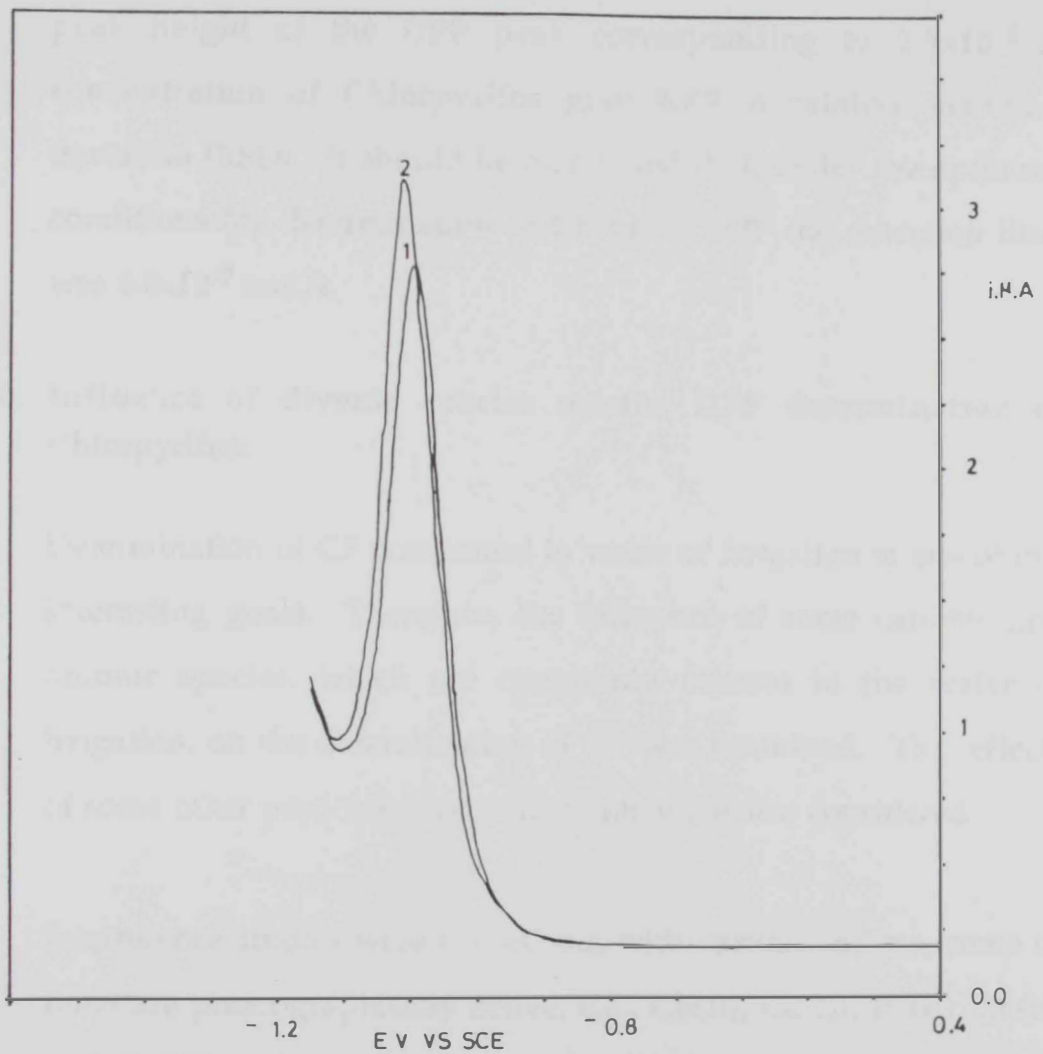


Fig. 3.11. : Dependence of the DPP peak of $5x10^{-5}$ mol/L CP on the drop time at pH 2.2. (1) 0.8 s and (2) 1.4 s.

($0.99x10^{-6}$ - $6.54x10^{-6}$ mol/l) of CP under the above mentioned conditions. The variation of the peak height of DPP response with the concentration of CP is linear (Fig. 3.12). The result of the calibration straight line was subjected to the least square refinement. It was found that the straight line has a regression coefficient (r^2) 0.995, slope $9.4x10^{-4}$ $\mu A/mol^{-1}$ and an intercept of 0.005 ± 0.002 μA. The results of five replicate measurements of the peak height of the DPP peak corresponding to $2.5x10^{-6}$ M concentration of Chlorpyrifos give 4.7% a relative standard deviation (RSD). It should be mentioned that, under the optimum conditions for determination of CP using DPP the detection limit was $6.0x10^{-7}$ mol/l.

3.1.6. Influence of diverse species on the DPP determination of Chlorpyrifos:

Determination of CP compound in water of irrigation is one of our interesting goals. Therefore, the influence of some cationic and anionic species, which are commonly present in the water of irrigation, on the determination of CP was examined. The effects of some other pesticides and surfactants were also considered.

Interference studies were carried out with various cations, some of them are polarographically active, e.g., Cu(II), Cd(II), Pb(II), Zn(II) and Cr(VI) and some polarographically inactive, e.g., Ca^{2+}, and Mg^{2+}. The effect of different anions which are more likely present in water of irrigation, e.g., NO_3^-, SO_4^{-2}, Cl^-, $Cr_2O_7^{-2}$, I^- and F^- were also, critically investigated.

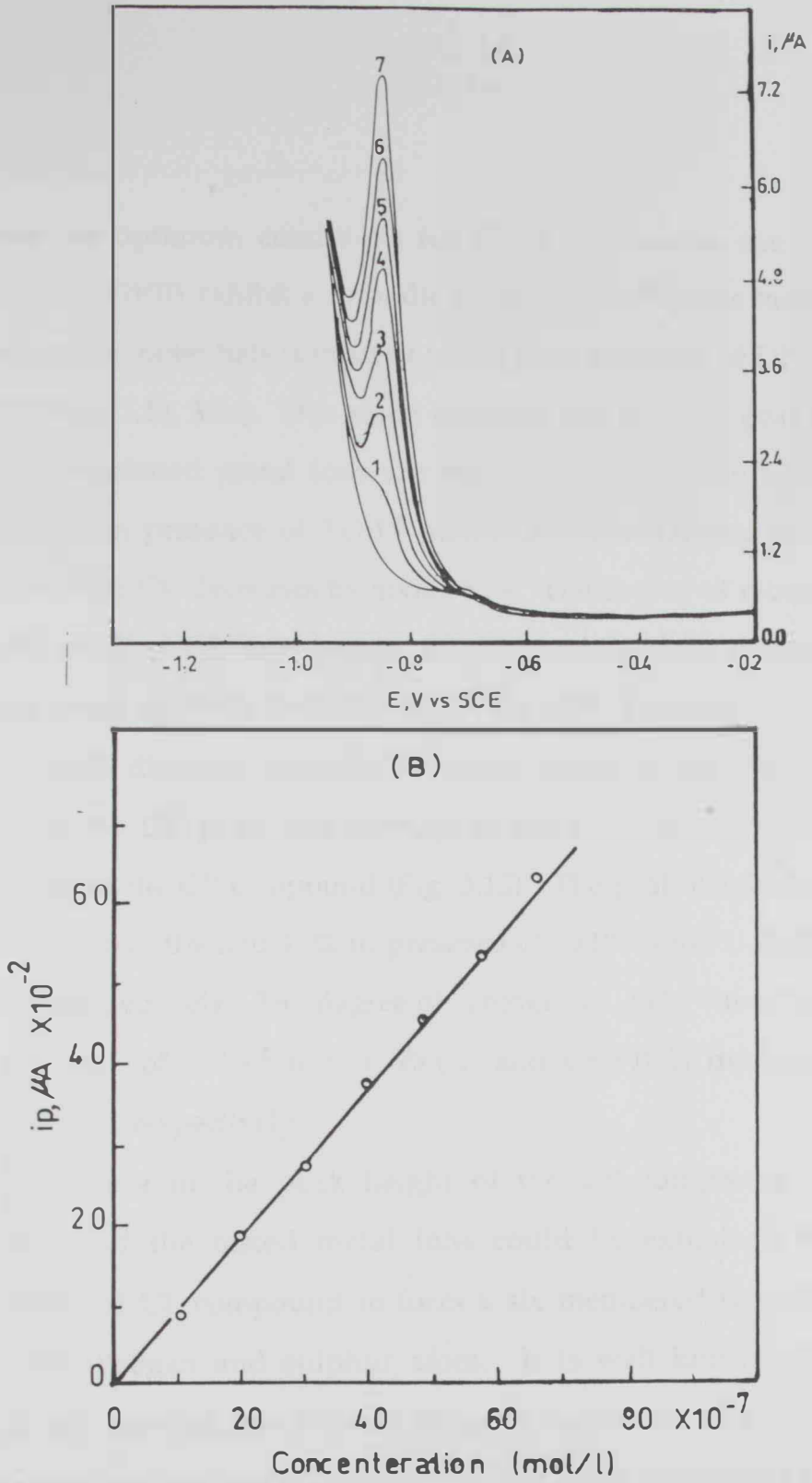


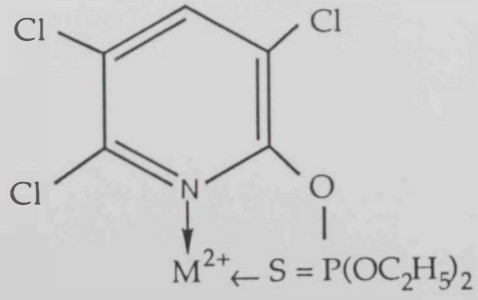
Fig. 3.12 (A) : The DP-polarograms of the various concentrations of CP at the selected optimum conditions.

(1) 0.99×10^{-6} , (2) 1.96×10^{-6} , (3) 2.92×10^{-6} , (4) 3.85×10^{-6} , (5) 4.76×10^{-6} , (6) 5.66×10^{-6} and (7) 6.54×10^{-6} mol/L CP.

(B) Calibration curve plot for CP determination.

Under the optimum conditions for CP determination the Cu(II), Pb(II) and Cd(II) exhibit a cathodic reduction DPP peaks located at less negative potentials compared to the peak potential of DPP peak of CP (Figs. 3.13, 3.14). This result indicates that the DPP peak of the above mentioned metal ions are not overlap with the CP peak. However, in presence of $1x10^{-5}$ mol/L of the metal ions the peak height of the CP decreases by about 10%. The degree of recovery of $5x10^{-5}$ mol/l of CP, in presence of $1x10^{-5}$ mol/L of the metal ion is in the range of 90-98 % (Table 3.2). The DPP behaviour of Zn(II) and Cr(VI) displays cathodic reduction peaks at potentials very close to the DP peak and overlap to some extent with the DPP respones of the CP compound (Fig. 3.15). The peak height of CP is decreased by 10% and 16% in presence of $1x10^{-6}$ mol/L Zn(II) and Cr(VI), respectively. The degree of recovery of $5x10^{-6}$ mol/l of CP, in presence of $1x10^{-4}$ mol/L Zn(II) and Cr(VI) is decreased by 18 and 28%, respectively.

The decrease in the peak height of the CP compound in the presence of the tested metal ions could be explained by the tendency of CP compound to form a six membered ring chelates via the nitrogen and sulphur atom. It is well known that the metal ion complex has a lower diffusion coefficient relative to the free metal ion and consequently it exhibits a less DPP current.



Structure of the possible CP-metal ion complex.

Table 3.2 : Interfering effect of Cu(II), Pb(II), Cd(II), Zn(II) and Cr(III) cation on the DPP behaviour of $5x10^{-5}$ mol/L CP under the optimum conditions for determination.

Cation	Concentration mol/L	Conc. of CP mol/L		Recovery
		added	found	
Cd	$1x10^{-5}$	$5x10^{-5}$	$4.9x10^{-5}$	98 %
	$1x10^{-4}$	$5x10^{-5}$	$4.5x10^{-5}$	90 %
Zn	$1x10^{-5}$	$5x10^{-5}$	$4.5x10^{-5}$	90 %
	$1x10^{-4}$	$5x10^{-5}$	$4.1x10^{-5}$	82 %
Cu	$1x10^{-5}$	$5x10^{-5}$	$4.7x10^{-5}$	90 %
	$1x10^{-4}$	$5x10^{-5}$	$4.2x10^{-5}$	84 %
Cr	$1x10^{-5}$	$5x10^{-5}$	$4.2x10^{-5}$	84 %
	$1x10^{-4}$	$5x10^{-5}$	$3.6x10^{-5}$	72 %
Pb	$1x10^{-5}$	$5x10^{-5}$	$4.5x10^{-5}$	90 %
	$1x10^{-4}$	$5x10^{-5}$	$3.9x10^{-5}$	78 %

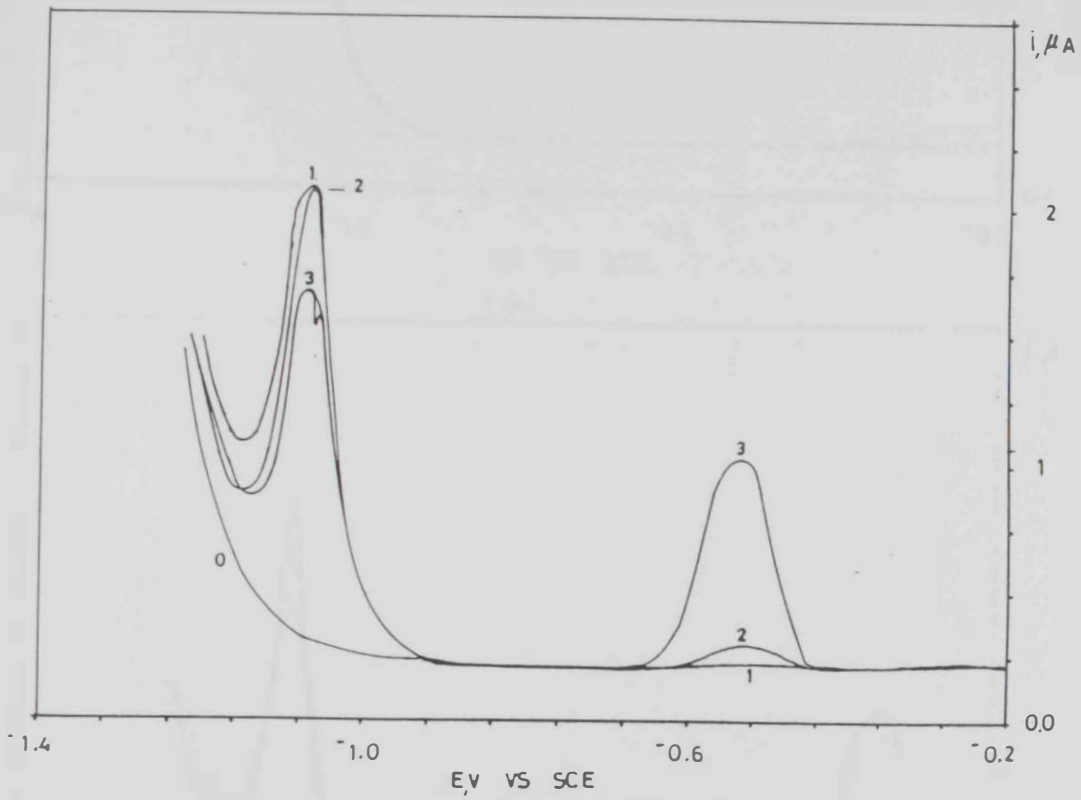


Fig. 3.13. : DPP behaviour of $5x10^{-5}$ mol/L CP under the optimum conditions in presence of (1) 0.0 , (2) 1.0 x 10^{-5} and (3) $1x10^{-4}$ mol/L Cd(II).

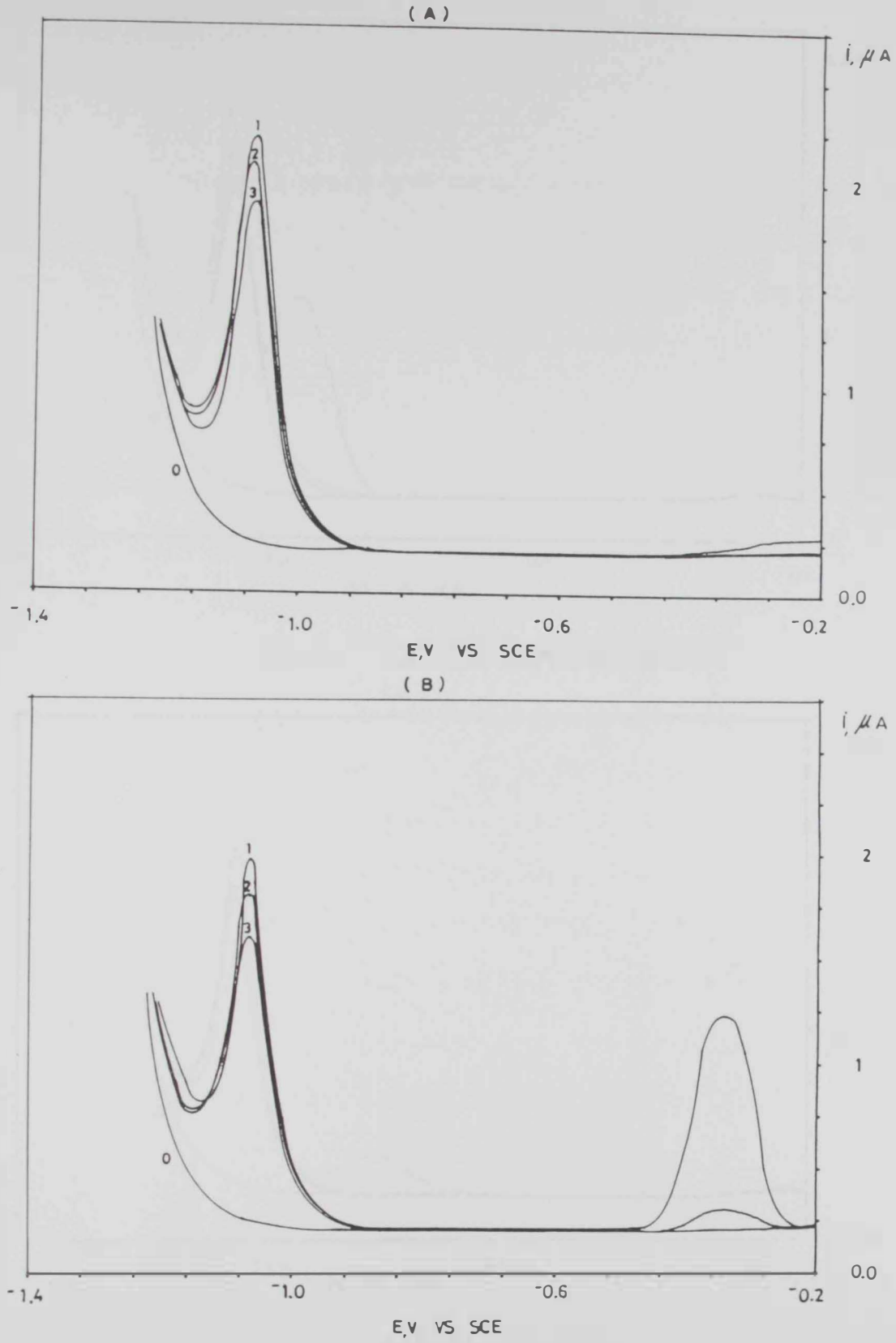


Fig. 3.14. : DPP behaviour of 5×10^{-5} mol/L CP in presence of:
[A] (1) 0.0 , (2) 1×10^{-5} and (3) 1×10^{-4} mol/L Cu(II) and
[B] (1) 0.0 , (2) 1×10^{-5} and (3) 1×10^{-4} mol/L Pb(II).

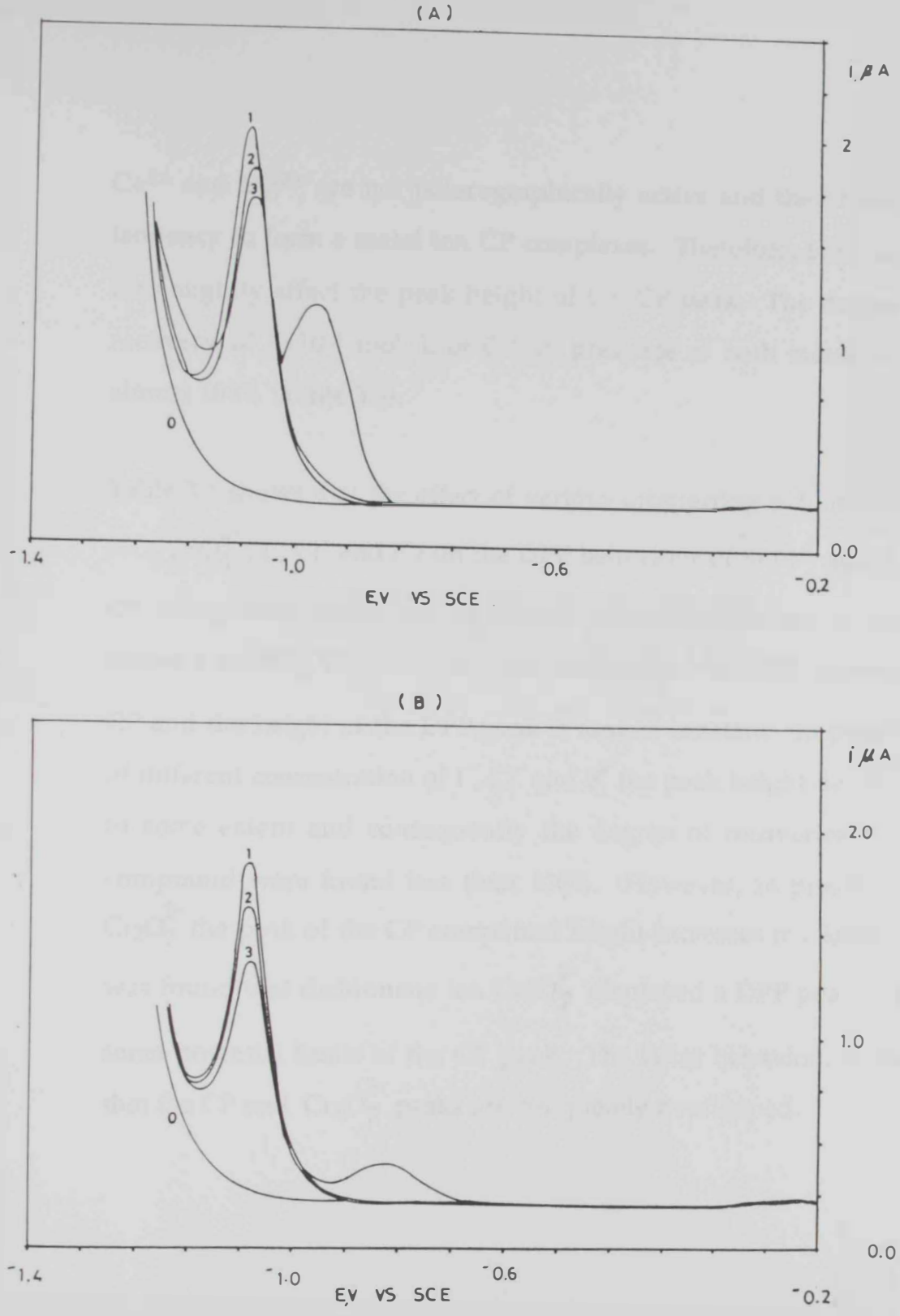


Fig. 3.15. : DPP behaviour of 5×10^{-5} mol/L CP in presence of:

[A] (1) 0.0 , (2) 1×10^{-5} and (3) 1×10^{-4} mol/L Zn(II) and

[B] (1) 0.0 , (2) 1×10^{-5} and (3) 1×10^{-4} mol/L Cr(II).

Ca^{2+} and Mg^{2+} are not polarographically active and they have no tendency to form a metal ion CP complexes. Therefore, both metal ions slightly affect the peak height of the CP peak. The degree of recovery of $5x10^{-5}$ mol/L of CP, in presence of both metal ion is almost 100% (Table 3.3).

Table 3.4 shows that the effect of various interferring anions (CO_3^{2-}, NO_3^-, SO_4^{2-}, I^-, Cl^- and F^-) on the DPP behaviour of $5x10^{-5}$ mol/L of CP compound under the optimum conditions. Some of these anions e.g., NO_3^-, CO_3^{2-} and SO_4^{2-} had no effect on the DPP current of CP and the height of the DPP peak is almost constant. In presence of different concentration of I^-, Cl^- and F^- the peak height decreased to some extent and consequently the degree of recoveries of CP compound were found less than 100%. However, in presence of $Cr_2O_7^{2-}$ the peak of the CP compound height increases markedly. It was found that dichromate ion $Cr_2O_7^{2-}$ displayed a DPP peak at the same potential limits of the CP peak. The latter behaviour reveals that the CP and $Cr_2O_7^{2-}$ peaks are completely overlapped.

Table 3.3 : Interfering effect of Ca^{2+} and Mg^{2+} on the DPP behaviour of $5x10^{-5}$ mol/L CP.

Anions	Concentration	Conc. of CP mol/L		Recovery
		added	found	
Ca	$1x10^{-5}$ $1x10^{-4}$	$5x10^{-5}$ $5x10^{-5}$	$4.9x10^{-5}$ $5x10^{-5}$	98 % 100 %
Mg	$1x10^{-5}$ $1x10^{-4}$	$5x10^{-5}$ $5x10^{-5}$	$5.15x10^{-5}$ $5.15x10^{-5}$	103 % 103 %

Table 3.4 : Interfering effect of anions on the DPP behaviour of $5x10^{-5}$ mol/L CP.

Anions	Concentration mol/L	Conc. of CP mol/L		Recovery
		added	found	
F^-	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ $5x10^{-5}$	$5x10^{-5}$ $4.5x10^{-5}$	100 % 90 %
NO_3^-	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ $5x10^{-5}$	$5x10^{-5}$ $4.8x10^{-5}$	100 % 98 %
CO_3^{2-}	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ $5x10^{-5}$	$5x10^{-5}$ $5x10^{-5}$	100 % 100 %
I^-	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ $5x10^{-5}$	$5.1x10^{-5}$ $4.9x10^{-5}$	102 % 98 %
SO_4^{2-}	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ $5x10^{-5}$	$5x10^{-5}$ $4.9x10^{-5}$	100 % 98 %
Cl^-	$1x10^{-4}$ $1x10^{-3}$	$5x10^{-5}$ 5x10-5	$4.7x10^{-5}$ 4.4x10-5	94% 88%

3.1.7. Influence of malathion and diazinon pesticides on the DPP behaviour of Chlorpyrifos:

The DPP behaviour of $5x10^{-5}$ mol/L of CP was investigated in the presence of various concentrations ($1x10^{-4}$ - $5x10^{-5}$ mol/L) of malathion and diazinon pesticides. The latter compounds are polarographically inactive and consequently they are not showing a differential pulse current. It was found that both compounds did not interfere with the DPP behaviour of CP and the degree of recovery of the DPP current of $5x10^{-5}$ mol/L of CP was 100% in presence of malathion and/or diazinon pesticides.

3.1.8. Analytical application of the DPP method for determination of Chlorpyrifos in some environmental samples:

Under the selected optimum conditions for determination of CP using DPP, the method was applied for the analysis of the CP in the commercial formulations in the sale market. Fig. 3.16 shows the DP polarograms of the CP at various concentration prepared from the commercial sample. The concentrations dependence of the peak height of the DPP commercial sample peak is linear over conc. range of $1.01x10^{-5}$ - $4.20x10^{-5}$ mol/L with degree of recovery, comprising to the standard calibration curve, was ranged from 95.8-103.6%. Also, the registered concentration on the data sheet of the commercial sample was recovered by 95.8%.

The analytical determination of CP compound in some water samples e.g. tape water, underground water and treated wastewater was examined. The concentration dependence of the DPP peak of

the CP, prepared in one of the above water type, was linear over a concentration range of $1x10^{-5}$ - $5x10^{-5}$ mol/L. Table 3.5 shows the degree of recoveries of CP solutions concentration prepared from the commercial and pure samples in different environmental water samples. The listed degree of recoveries (Table 3.5) are in the acceptable range, whereas for a pure or commercial sample prepared in the underground water the degree of recovery is relatively low at lower concentrations of CP. These results indicate that the interfering ions in the different water types were not highly affecting the method of determination of CP using DPP.

The proposed DPP method for CP determination was applied for determination of the extracted CP from the surface of tomatoes plant (CP was collected from the surface of 1 kg tomatoes using extraction technique). Many trials were made for CP determination in the extracted sample and all of them were not succeeded. This could be explained that the concentration of the extracted CP was lower than that of the detection limit of DPP technique.

Table 3.5 : Degree of recoveries of the CP solutions prepared from the commercial and pure samples in different environmental water samples.

Sample	Concentration of CP	Recovery
Commercial sample in bi-distilled water	$1.01X10^{-5}$ - $4.20 X 10^{-5}$	95.8 - 103.6%
Pure sample in tap water	$1.01x10^{-5}$ - $4.20x10^{-5}$	93.2 - 97.0%
Pure sample in treated wastewater	$1.01x10^{-5}$ - $4.20x10^{-5}$	94.6 - 104.1%
Pure sample in underground water	$1.01x10^{-5}$ - $4.20x10^{-5}$	83.0 - 91.6%
Commercial sample in underground water	$1.01x10^{-5}$ - $4.20x10^{-5}$	81.0 - 90.6%

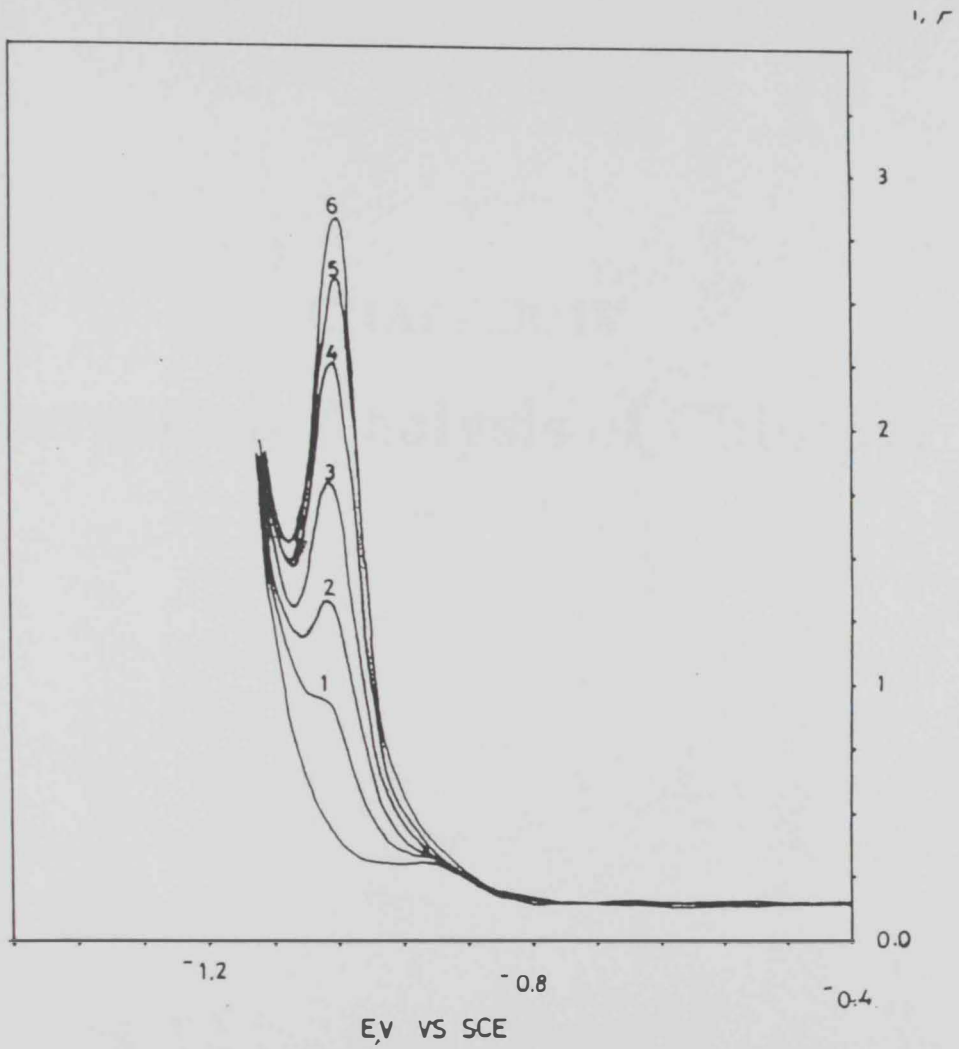


Fig. 3.16. : DP-polarograms of various concentrations prepared from the commercial sample, under the optimum conditions. (1) 1.01×10^{-5} , (2) 1.86×10^{-5} , (3) 2.58×10^{-5} , (4) 3.20×10^{-5} , (5) 3.73×10^{-5} and (6) 4.20×10^{-5} mol/L CP.

CHAPTER IV

Voltammetric Analysis of Chlorpyrifos

4.1. Cyclic Voltammetric Behaviour of Chlorpyrifos (CP) at the Hanging Mercury Electrode

The oxidation/reduction behaviour of Chlorpyrifos (CP) was studied using cyclic voltammetric technique at the hanging mercury drop electrode (HMDE). A further aim of this study is the investigation of the adsorption and accumulation of the investigated compound at the charged mercury electrode surface as a prerequisite step for cathodic adsorptive stripping analysis step.

The cyclic voltammetry of CP as a function of potential was investigated in solutions of varying pH and represented in Fig. 4.1. The CV behaviour indicate two cathodic peaks. The first peak is reversible peak and located at potential's close to 0.0V and the second one is irreversible peak and appeared at more negative potentials close to H^+ discharge potential. The first peak represents a common CV behaviour of sulphur containing compounds (Temerk and others, 1992) and corresponding to the redox behaviour of the Hg^{2+}-thiolate film which may be formed at the polarized mercury electrode surface. The reversible redox process of the first peak could be represented by the following equation:

$$Hg + RS \rightleftharpoons Hg(RS)_2 + 2e^-$$

However, the second irreversible cathodic peak is probably corresponding to the irreversible reduction of the $\rangle C = N$ of the pyridyl moiety via the $2e^-/2H^+$ mechanism.

The cyclic voltammograms of CP compound at various scan rates are recorded at pH 3.0 as shown in Fig. 4.2. The CV peak height increases with increasing the scan rate from 20 to 200 mV/s. The cathodic peak potential was found to shift in the negative direction with increasing the scan rate. This result reveals that the degree of irreversibility increases with increasing the scan rate. It should be mentioned that at very fast scan rate e.g., 200 mV/s, an anodic spike was observed at potential identical to the potential of the cathodic peak. This indicates that the weak adsorption of the reduction product relative to the strong adsorption of the oxidized form at the mercury surface. Therefore, the reoxidation process could be observed at fast scan only before the desorption of the reduced form from the electrode surface. This result supports the strong adsorption and accumulation of the oxidized form of CP at the mercury electrode surface.

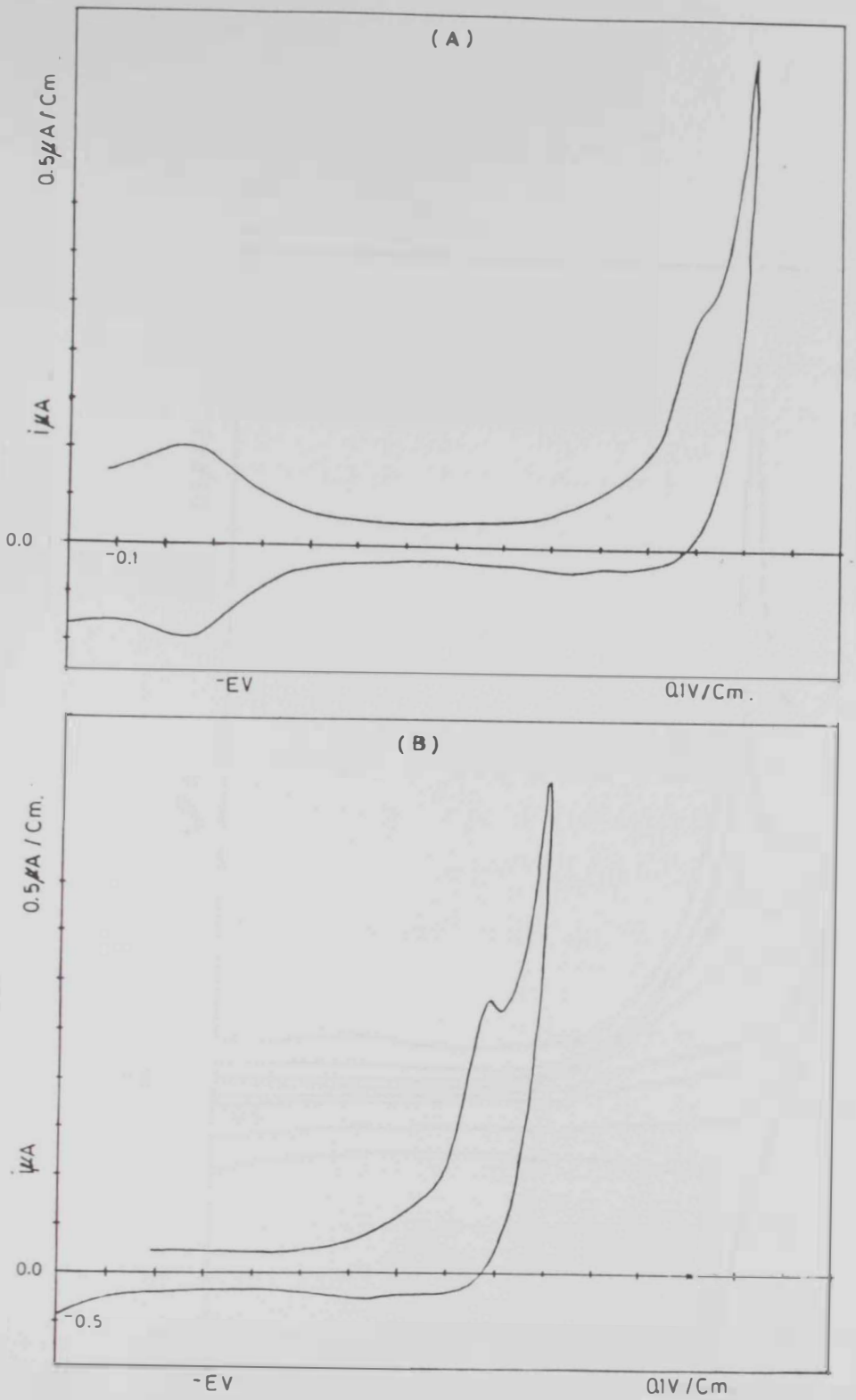


Fig. 4.1. : Cyclic voltammetric behaviour of $5x10^{-6}$ mol/L CP. (A) pH 2.2 and (B) pH 6.02.

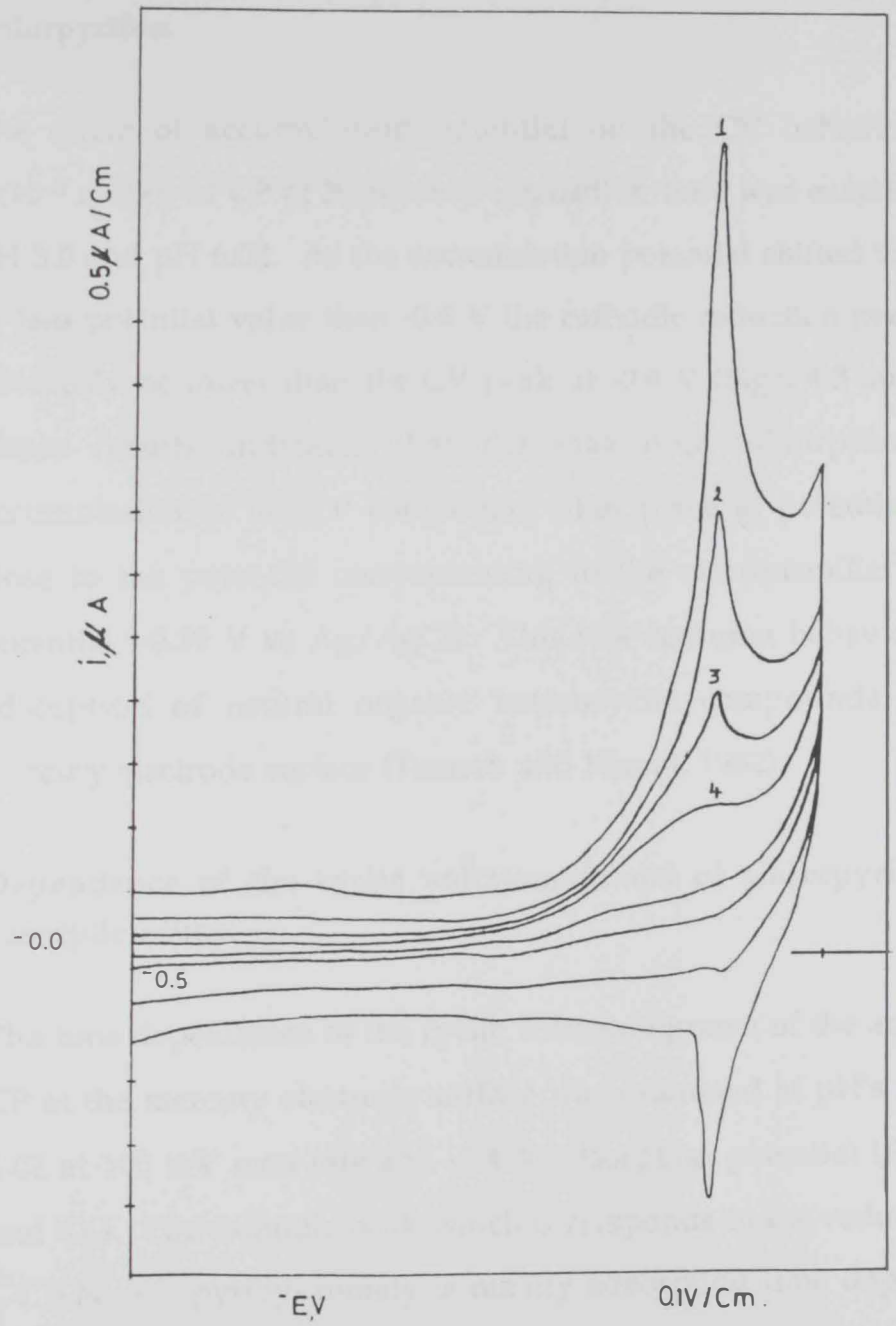


Fig. 4.2. : CV voltammograms of 5×10^{-6} mol/L CP at pH 3.0 at different scan rates.

1) 200 , 2) 100 , 3) 50 and 4) 20 mV/s.

4.1.1. Effect of adsorption potential on the cyclic voltammograms of Chlorpyrifos:

The effect of accumulation potential on the CV behaviour of $5x10^{-6}$ mol/L of CP at 30 seconds deposition time was examined at pH 3.0 and pH 6.02. As the accumulation potential shifted to more or less potential value than -0.4 V the cathodic reduction peak will obviously be lower than the CV peak at -0.4 V (Figs. 4.3 and 4.4). These results indicates that the maximum adsorption and accumulation of the CP compound takes place at potential very close to the potential corresponding to the electrocapillary zero potential (-0.39 V vs Ag/AgCl). This is a common behaviour for adsorption of neutral organic heterocyclic compounds at the mercury electrode surface (Temerk and Kamal, 1982).

4.1.2. Dependence of the cyclic voltammograms of Chlorpyrifos on adsorption time:

The time dependence of the cyclic voltammograms of the adsorbed CP at the mercury electrode surface was examined at pH's 3.0 and 6.02 at 100 mV scan rate and -0.4 V adsorption potential (Figs. 4.5 and 4.6). The cathodic peak which corresponds to the reduction of $\rangle C = N -$ of pyridyl moiety is mainly adsorption time dependent. The peak height (i_p, μA) increases with the adsorption time up to 180 s indicating that the amount of adsorbed species increases with time and the maximum surface coverage of the electrode occurs at 180 s.

It should be mentioned that the cyclic voltammetric behaviour of CP was carried out in relatively dilute solution of CP ($1x10^{-6}$ mol/L) and at higher scan rate (100-200 mV s^{-1}) in order to enhance the CP adsorption current relative to the diffusion controlled ones. The above results confirm that the faradaic cathodic reduction CV peak of the CP compound, which appeared as the result of the adsorbed species at the mercury electrode surface, is relatively high and well separated from the hydrogen discharge potential. Also, the above results show that the CP compound is adsorbed and accumulated at the charged mercury electrode surface. A controlled adsorption of CP at the Hg surface provides the basis for direct stripping measurements at a very low concentration range.

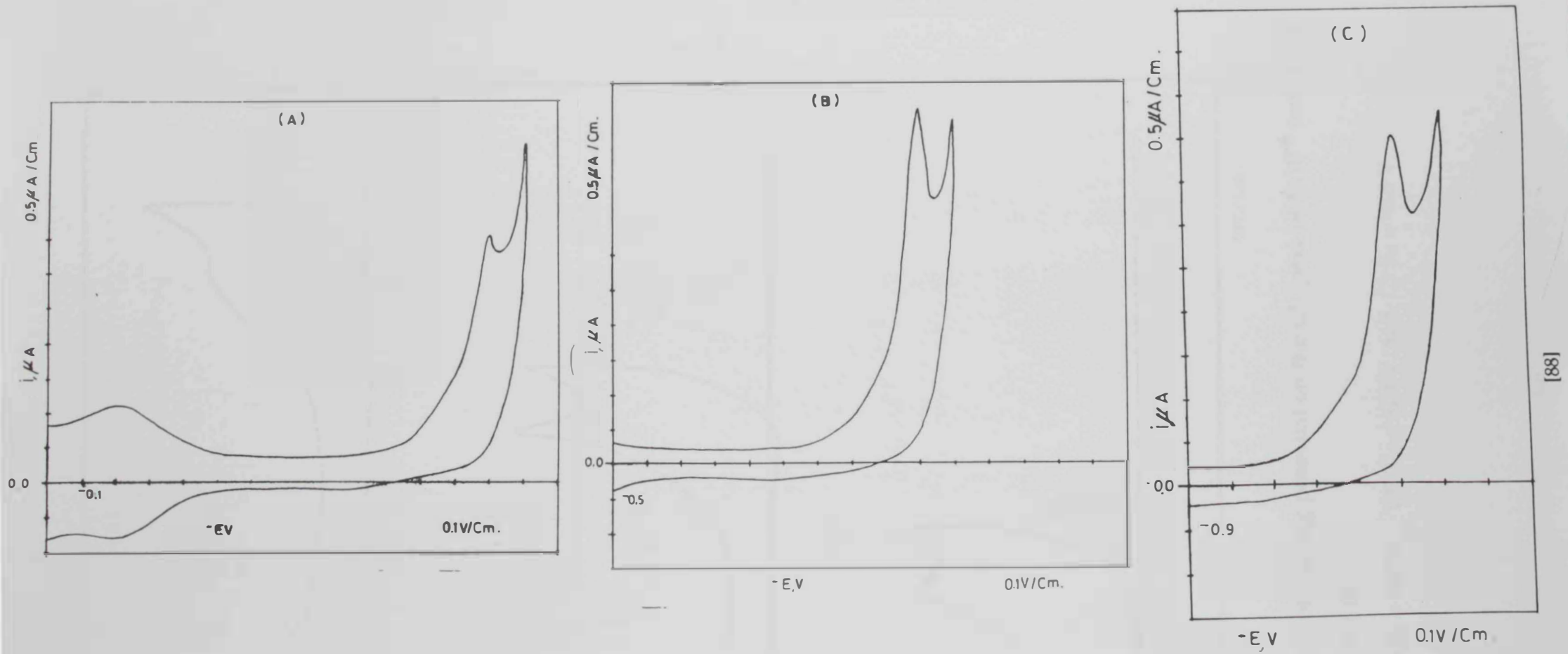


Fig. 4.3. : Effect of starting potential on the CV peak of 5×10^{-6} mol/L CP at pH 3.0.

(A) E_s = 0.0 V , (B) E_s = -0.4 V and C) E_s = -0.8 V.

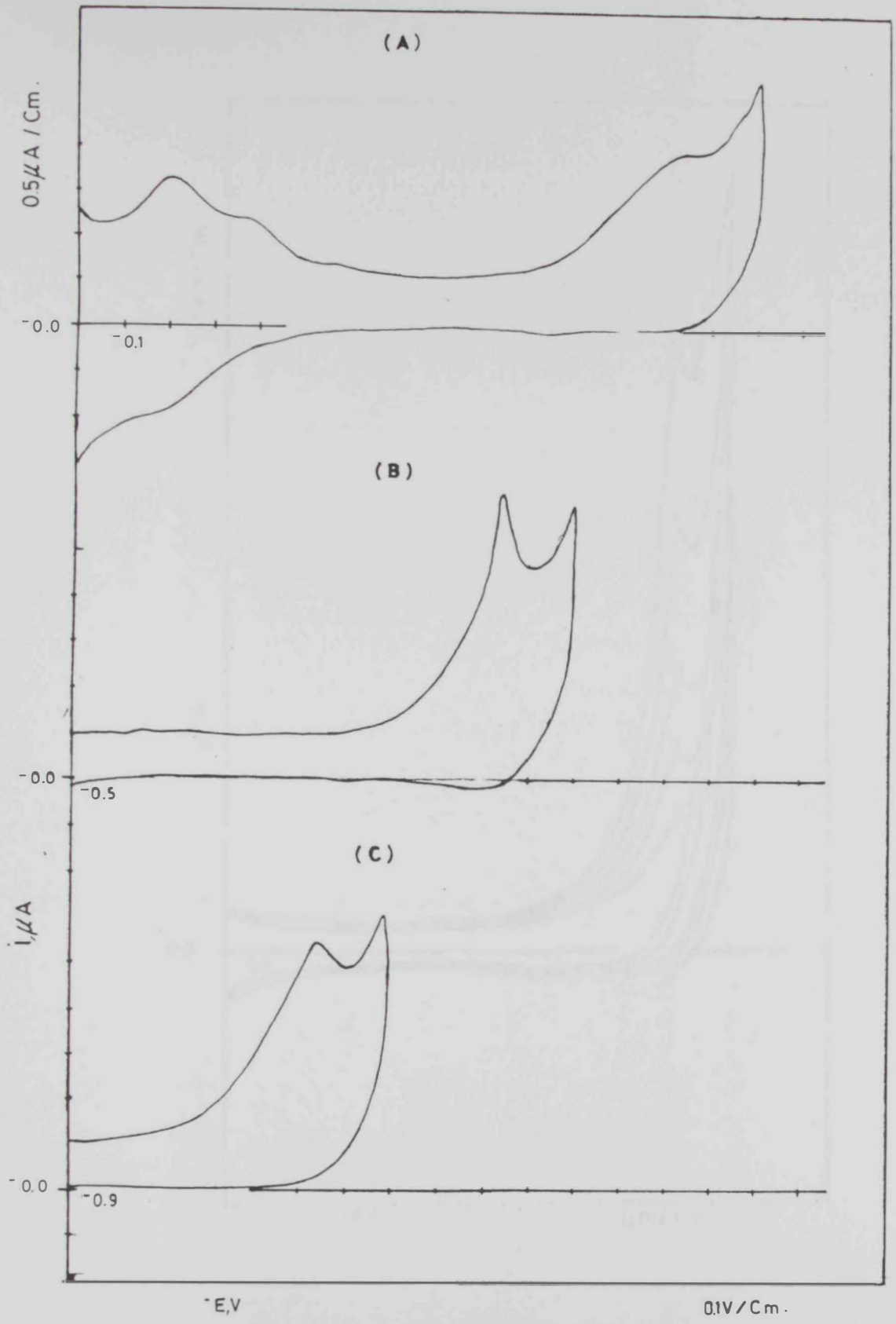


Fig. 4.4. : Effect of starting potential on the CV peak of 5×10^{-6} mol/L CP at pH 6.02

(A) E_s = 0.0 V , (B) E_s = -0.4 V and C) E_s = -0.8 V.

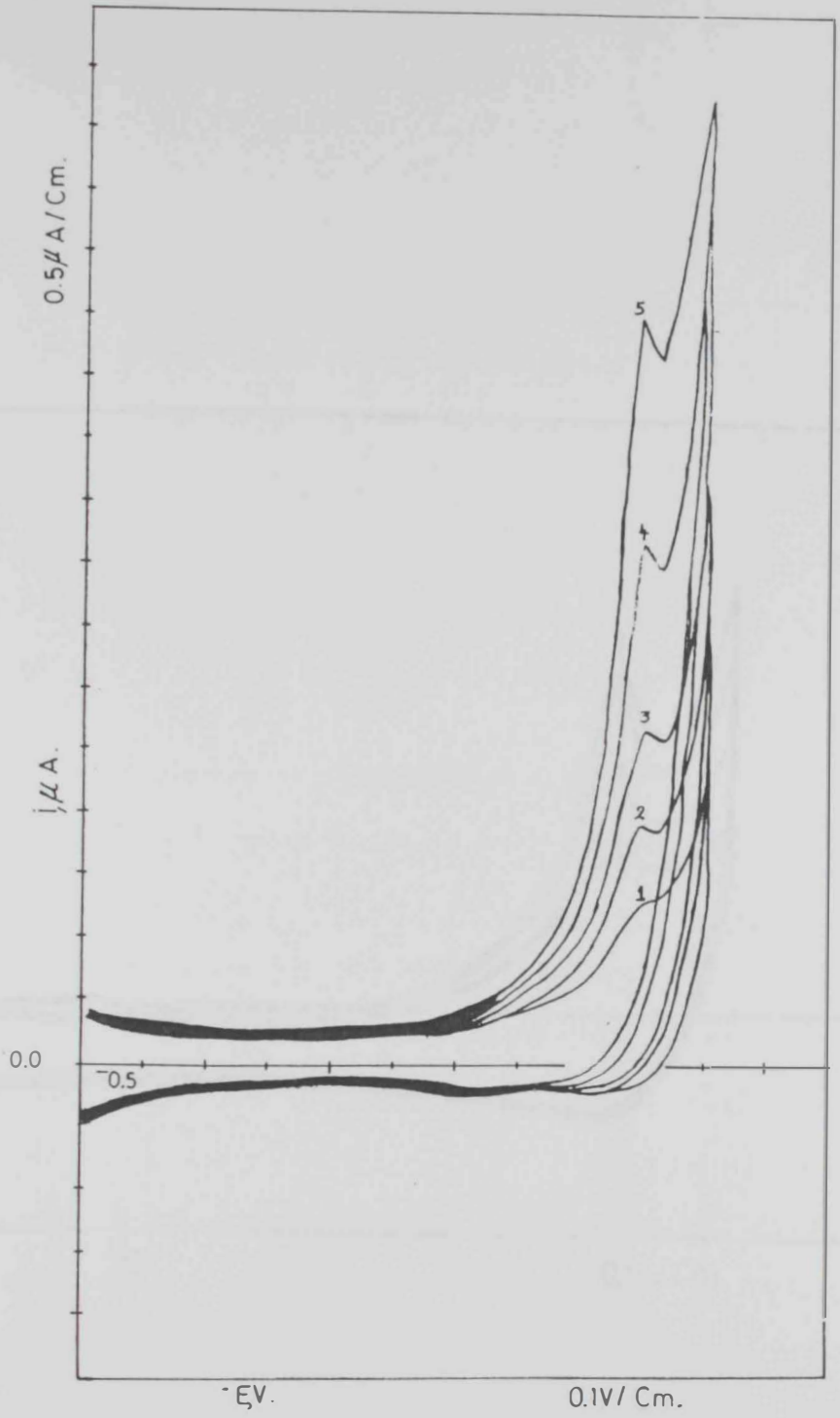


Fig. 4.5. : Adsorption time dependence of the CV peak of $5x10^{-6}$ mol/L CP at pH 3.0.

1) 0.0 , 2) 30 , 3) 60 , 4) 120 and 5) 180 Sec.

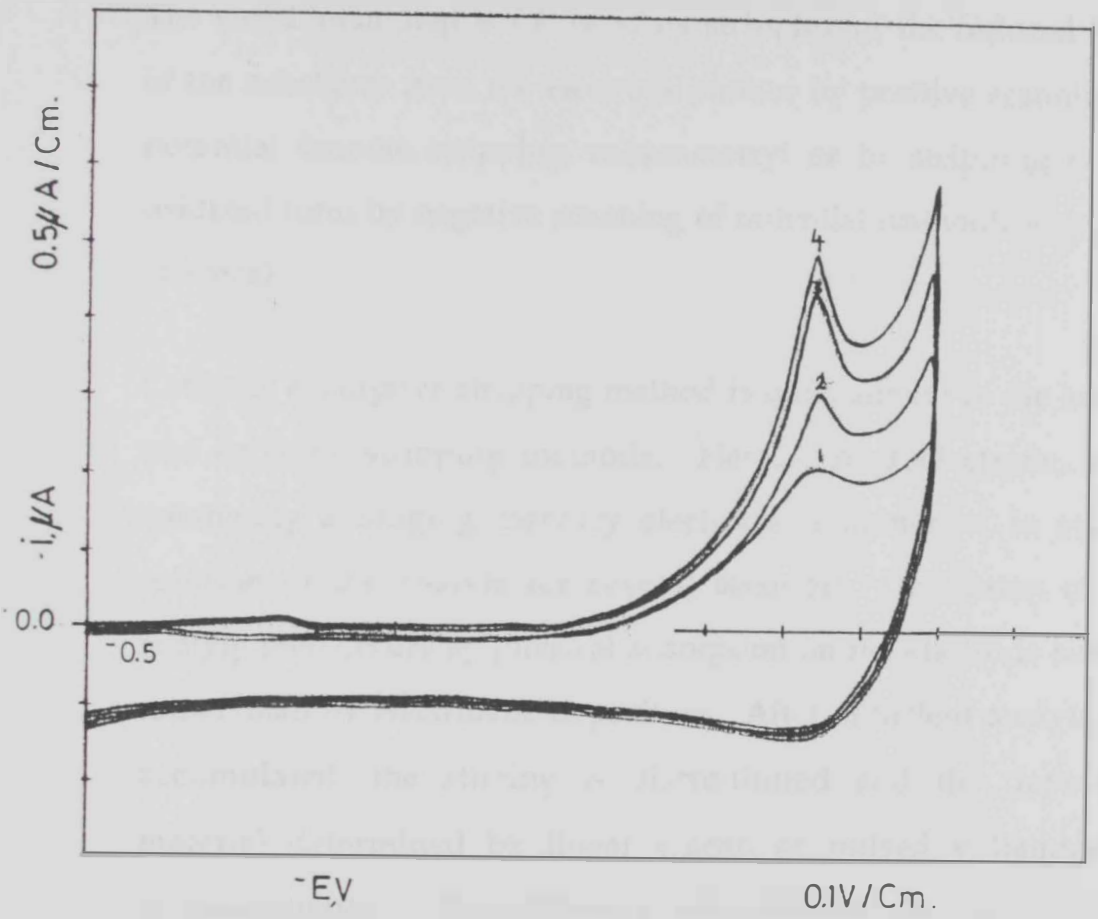


Fig. 4.6. : Adsorption time dependence of the CV peak of 5×10^{-6} mol/L CP at pH 6.02.

1) 0.0 , 2) 60 , 3) 120 and 4) 180 Sec.

4.2. Cathodic Adsorptive Stripping Voltammetric Analysis of Chlorpyrifos

A considerable increase in the sensitivity of the voltammetric method of analysis can be obtained by enrichment of the substance to be determined prior to the polarographic or voltammetric determination itself, usually by electrolysis at a stationary electrode. The enrichment step is followed by stripping of the reduced form of the substance from the electrode surface by positive scanning of potential (anodic stripping voltammetry) or by stripping of the oxidized form by negative scanning of potential (cathodic stripping analysis).

Cathodic adsorptive stripping method is quite similar to the anodic and cathodic stripping methods. Here, a microelectrode, most commonly a hinging mercury electrode is immersed in stirred solution of the analyte for several seconds. Deposition of the analyte then occurs by physical adsorption on the electrode surface rather than by electrolytic deposition. After sufficient analyte has accumulated, the stirring is discontinued and the deposited material determined by linear - scan or pulsed voltammetric measurements. Quantitiative information is based upon calibration with standard solutions that are treated in the same way as samples.

Many organic molecules of clinical, pharmaceutical (Ahmed and others, 1994) and pesticidal (Kamal and others, 1996) interest have a strong tendency to be adsorbed from aqueous solutions onto a mercury surface, particularly if the surface is maintained at about

-0.4 V vs SCE where the charge on mercury is zero. Cathodic adsorptive stripping voltammetric (CASV) method is very sensitive especially when it coupled with differential pulse (DP) technique. The limit of detection of the analyte is strongly depends on the operation and experimental conditions and is very close to 10^{-9} - 10^{-8} mol/L.

4.2.1. General voltammetric behaviour of Chlorpyrifos:

The cathodic adsorptive stripping (CAS) voltammograms of CP were recorded over a wide pH range (3.0-9.2) in Britton-Robinson buffer solutions containing 25% ethanol using differential pulse voltammetry (DPV).

The adsorbed oxidized form of CP molecules exhibit only a CAS reduction peak, which is pH dependent (Fig. 4.7). This peak is corresponding to the reduction of the $\rangle C = N$ - centre of the pyridyl moiety of CP compound via the $2e^-/2H^+$ reduction mechanism. In relatively strong acid solutions (pH $\leq$ 4.2), this reduction peak was completely overlapped with back ground discharge. The latter behaviour is probably due to the highly catalytic effect of the investigated compound on the H^+ discharge. In acidic solutions and at higher $[CP]/[H^+]$ ratios, ca 0.5 or more, the reduction peak is seen. However, this conditions is unsuitable for trace analysis of the investigated pesticide. In slightly acidic and neutral solution the cathodic reduction peak is well defined and pH sensitive even at very low concentration of CP ca $5x10^{-7}$ mol/L. The reduction peak shifts to more negative potentials and its height decreases

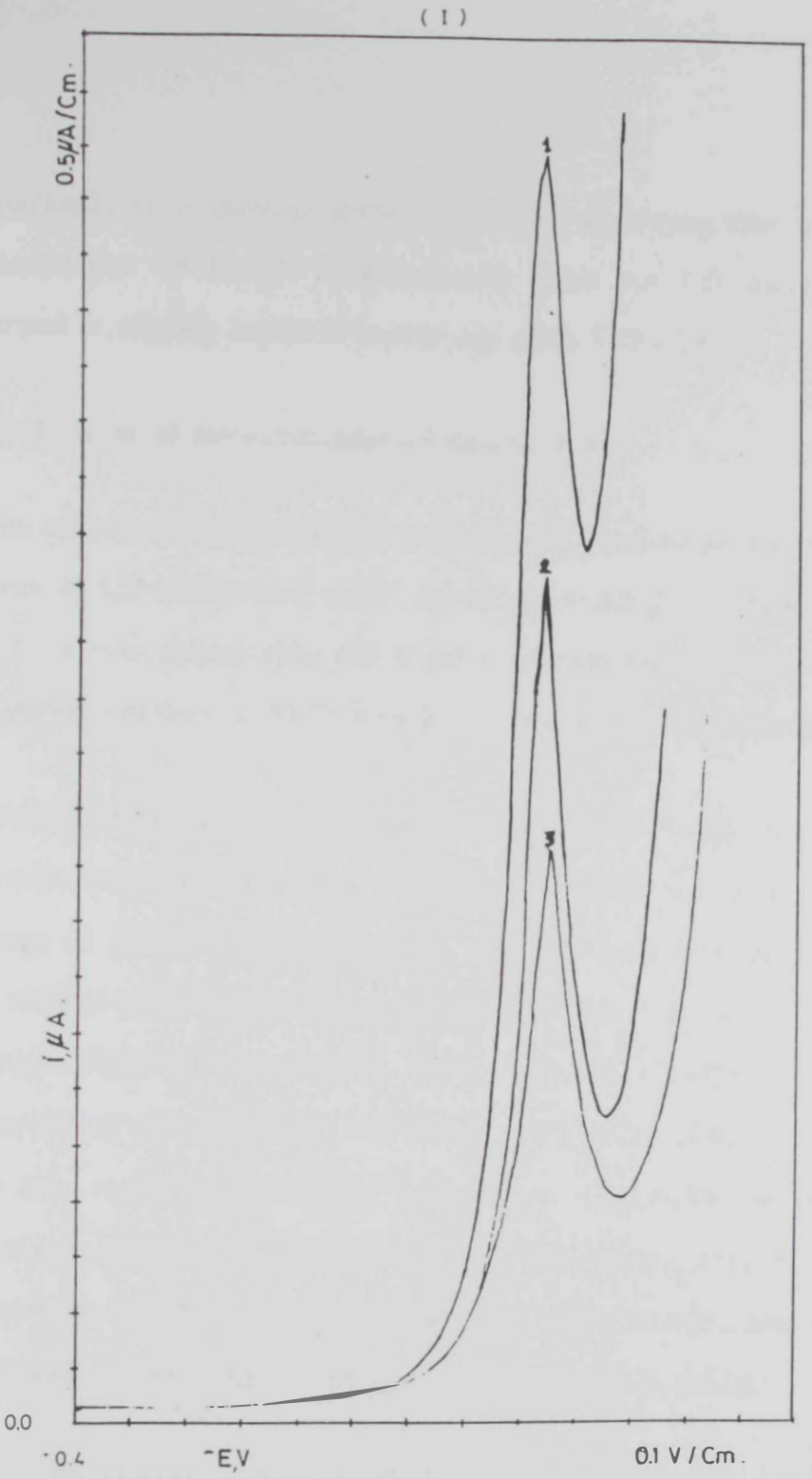


Fig. 4.7. : The pH dependence of the DP-CASV voltammograms of $5x10^{-6}$ mol/L CP.

1) pH 4.01 , 2) pH 5.02 and 3) pH 7.9.

markedly with increasing the pH of the supporting electrolyte. The maximum DP-CASV voltammetric peak for CP pesticide was found in slightly acidic solutions e.g. pH's 5.01 and 6.0.

4.2.2. Evaluation of the experimental parameters:

The effects of ionic strength and ethanol percent on the DP-CASV peak of CP compound were investigated at pH 5.1 (Figs. 4.8 and 4.9). It was found that the maximum response is reported for a solution containing 0.025 mol/L $NaNO_3$ and 25% of ethanol.

The dependence of the of the DP-CASV peak height of CP on the preconcentration potential was studied at pH 5.1 in the potential range of -0.2 to -0.8 V (Fig. 4.10). When the accumulation potential is shifted to more positive or negative value than -0.4 V, the peak height decreases markedly. This behaviour indicates that the maximum accumulation and adsorption of the tested compound at the mercury electrode surface is observed at potentials corresponding to the electrocapillary zero potential of the mercury electrode (-0.39 V vs Ag/AgCl). The accumulation potential was adopted at -0.4 V for the stripping analysis experiments.

The DP-CASV voltammograms of $1x10^{-6}$ mol/L of CP were recorded at various scan rates (Fig. 4.11) at pH 5.1. The height of the reduction peak increases with increasing the scan rate, however at higher scan rate (20 and 50 mV/s) the width of the peak increases and becomes less resolved. Hence a scan rate 10 mv/s was chosen for stripping voltammetry of the adsorbed CP at the mercury electrode surface.

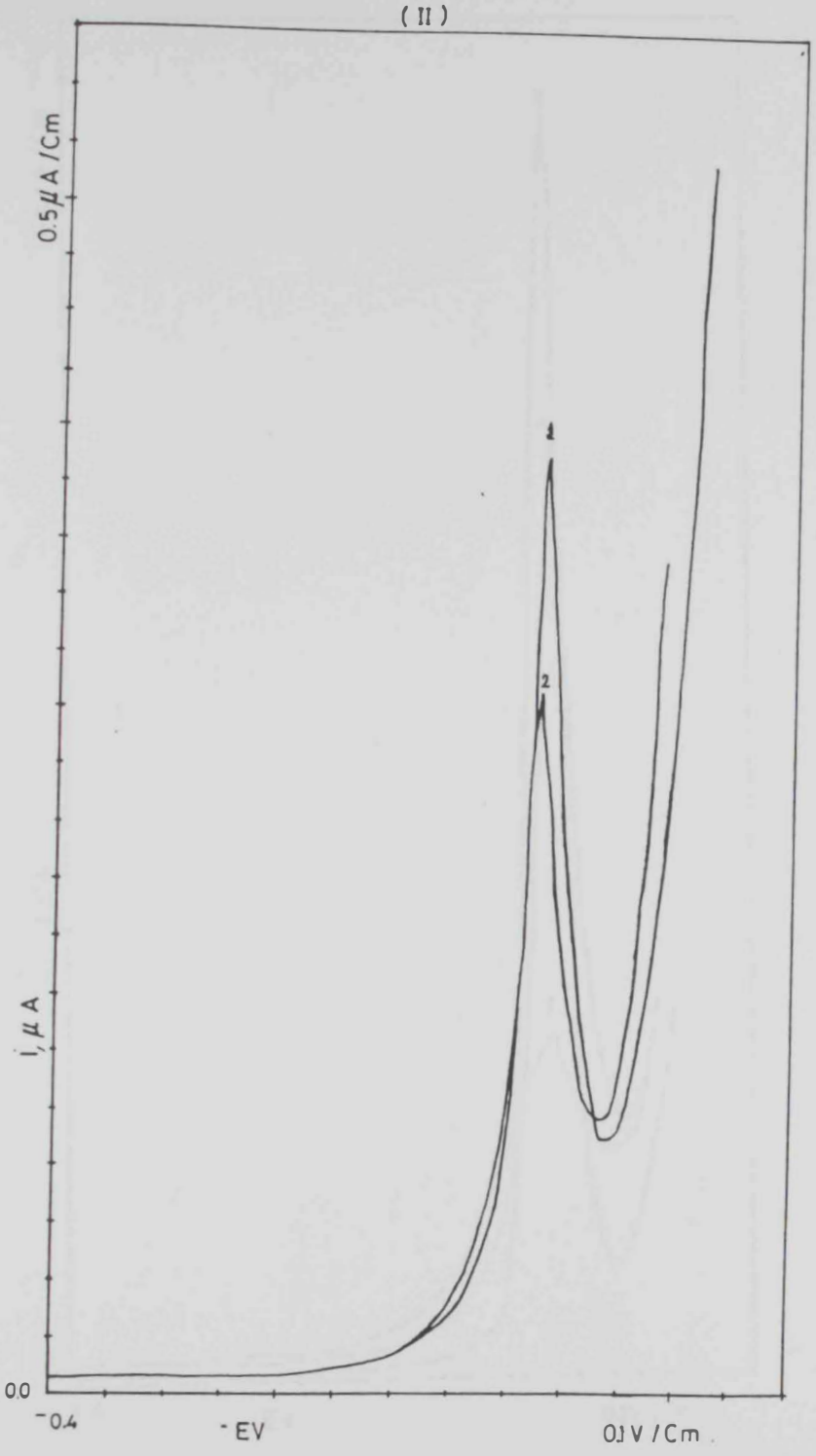


Fig. 4.8. : Effect of NO_3^- concentration on the DP-CASV peak of $5x10^{-6}$ mol/L CP at pH 5.01.
1) 0.025 and 2) 0.05 mol/L NO_3^-.

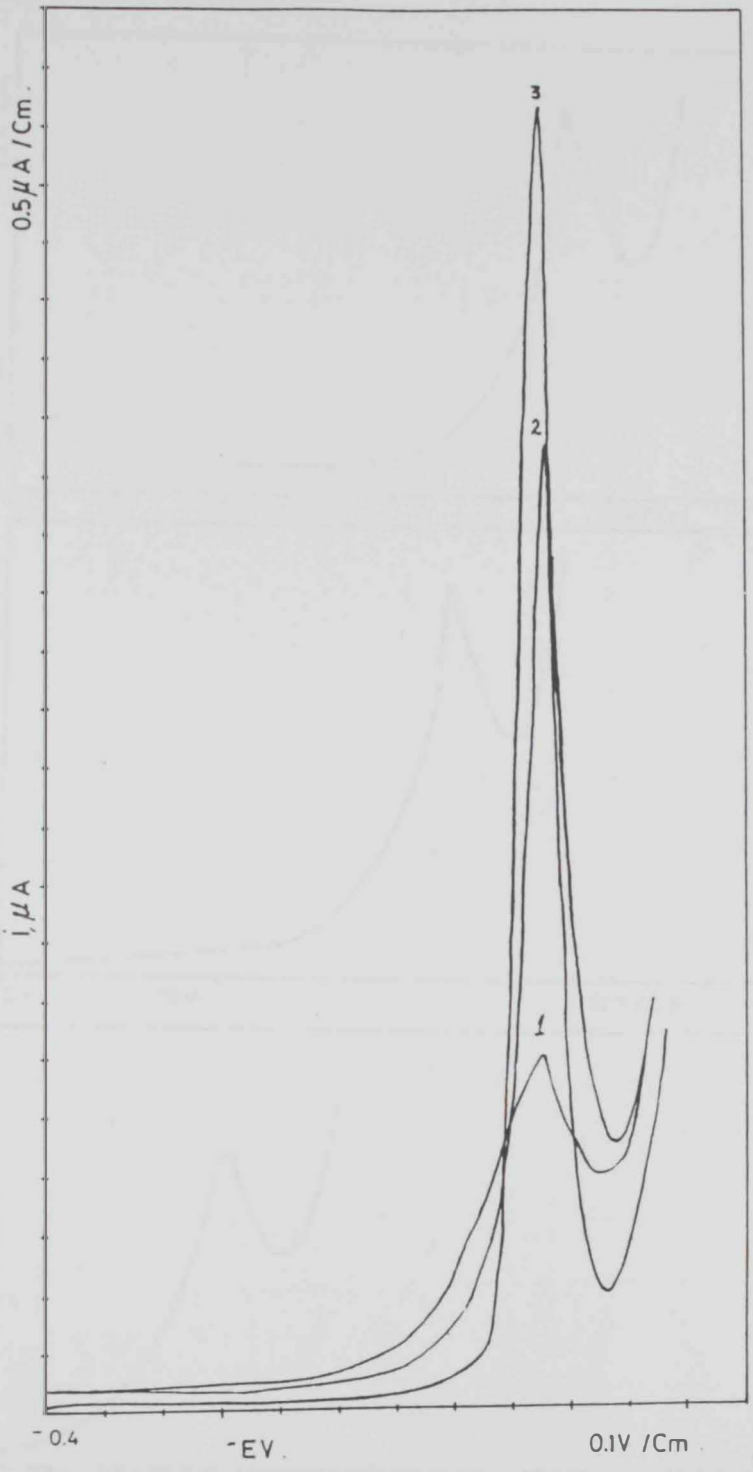


Fig. 4.9. : Effect of ethanol percentage on the DP-CASV peak of $5x10^{-6}$ mol/L CP at pH 5.01.

1) 10% , 2) 20% and 3) 25% ethanol.

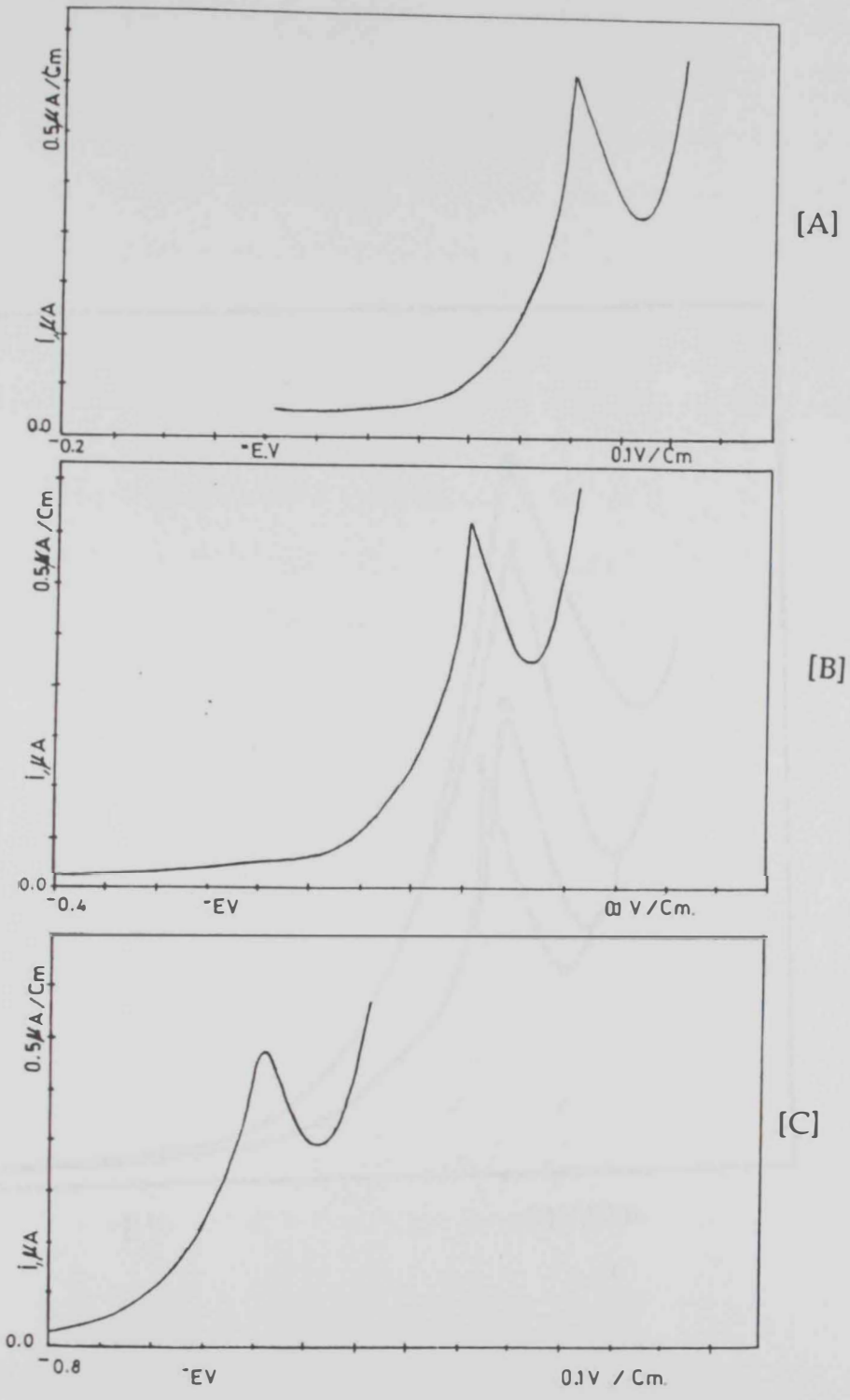


Fig. 4.10. : Effect of starting potential on the DP-CASV peak of 5×10^{-6} mol/L CP at pH 5.01.

(A) E_s = -0.2 V , (B) E_s = -0.4 V and (C) E_s = -0.8 V.

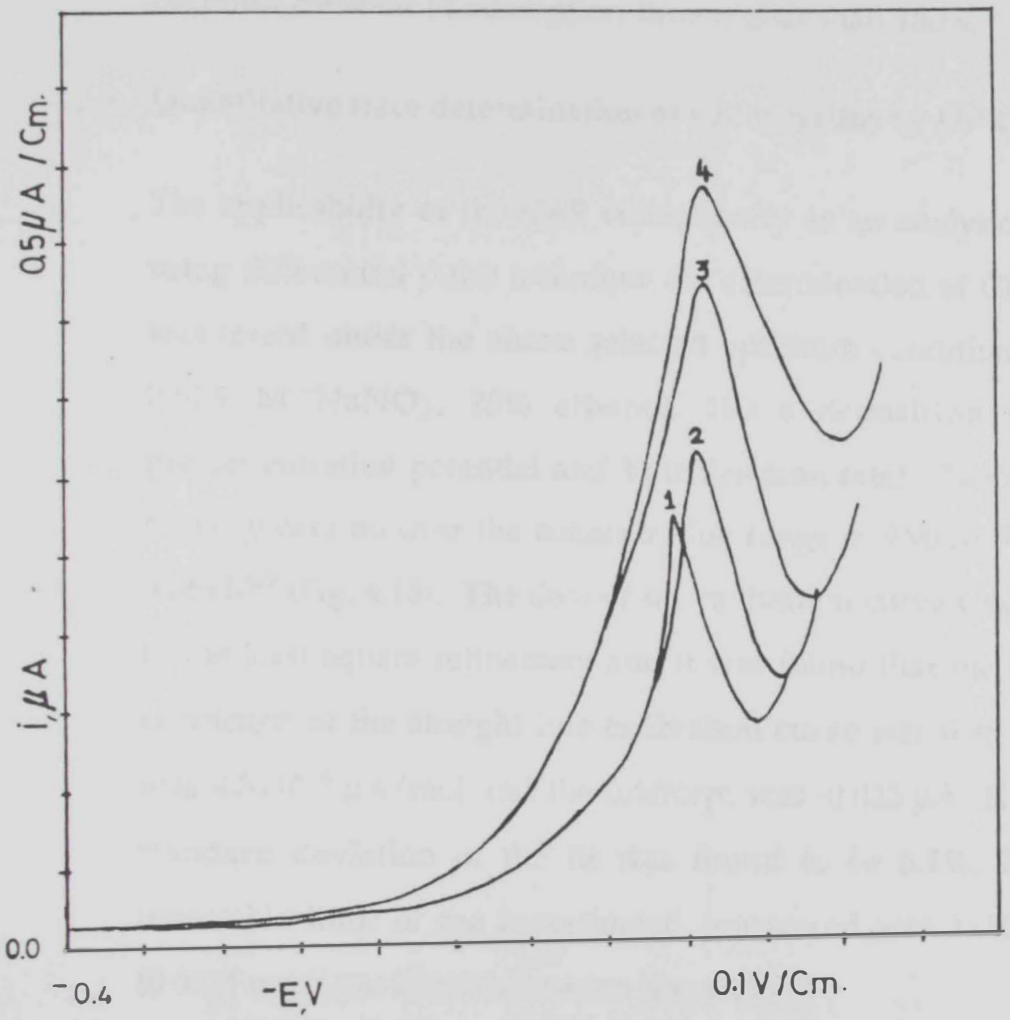


Fig. 4.11. : Effect of scan rate on the DP-CASV peak of 1×10^{-6} mol/L CP at pH 5.01.

1) 5 , 2) 10 , 3) 20 and 4) 50 mV/s.

The effect of the preconcentration time on the stripping peak height of the tested compound was followed at pH 5.1 (Fig. 4.12). The peak height of the reduction process of the adsorbed CP increases with increasing the adsorption time (t_s, sec.). An equilibrium surface concentration is reached and the peak height becomes constant at adsorption time higher than 180 s.

4.2.3. Quantitative trace determination of Chlorpyrifos by DP-CASV:

The applicability of the CAS voltammetry as an analytical method using differential pulse technique for determination of CP pesticide was tested under the above selected optimum conditions (pH 5.1, 0.025 M $NaNO_3$, 25% ethanol, 180 s deposition time, -0.4 preconcentration potential and 10 mV/s scan rate). The calibration curve generated over the concentration range of 9.90×10^{-8} mol/L to 5.66×10^{-7} (Fig. 4.13). The data of the calibration curve was subjected to the least square refinement and it was found that the regression coefficient of the straight line calibration curve was 0.98, the slope was 4.5×10^{-6} μA/mol and the intercept was -0.025 μA. The relative standard deviation of the fit was found to be 6.1%. The lower detectable limit of the investigated compound was 1×10^{-8} mol/L (0.0034 mg/L) at 300 s deposition time.

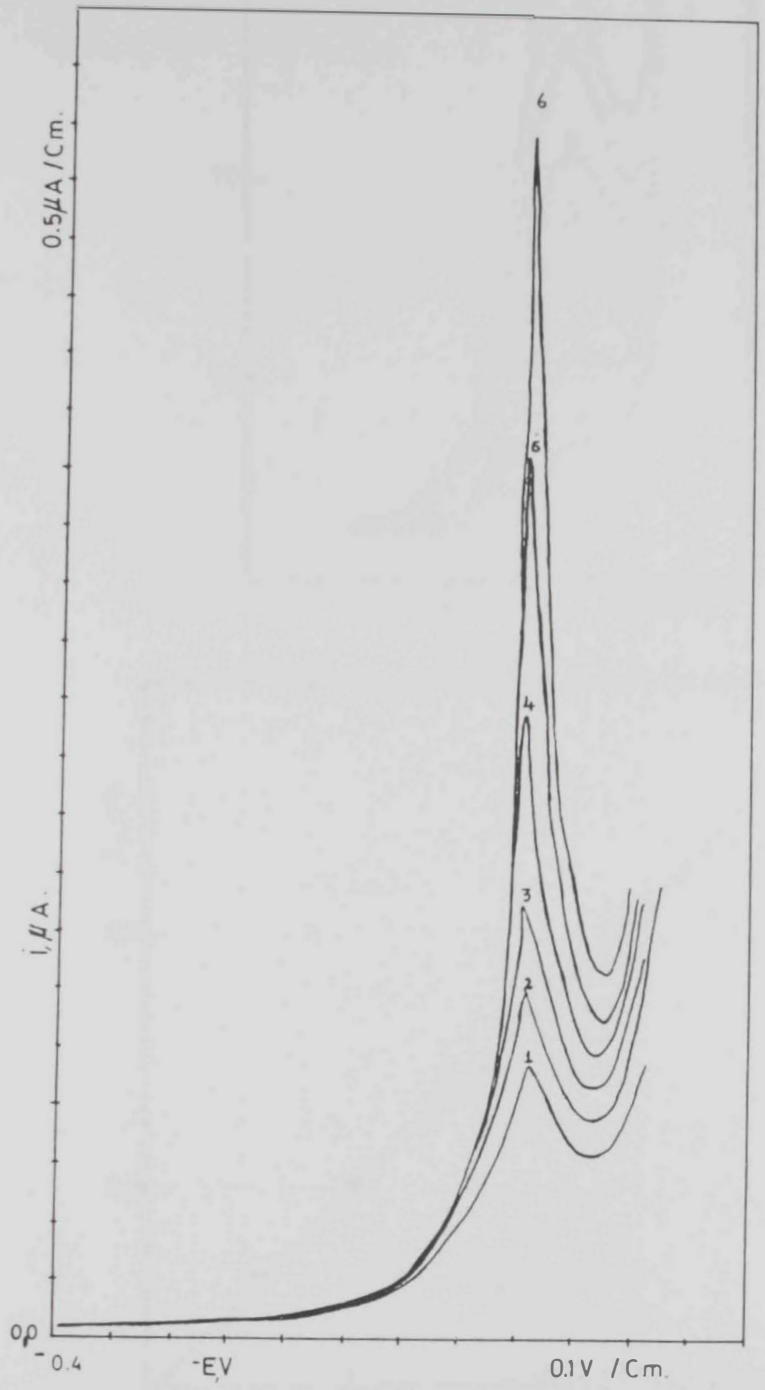


Fig. 4.12. : Adsorption time dependence of the 1×10^{-6} mol/L CP at pH 5.01.

1) 0 , 2) 30 , 3) 60 , 4) 90 , 5) 120 and 6) 180 Sec.

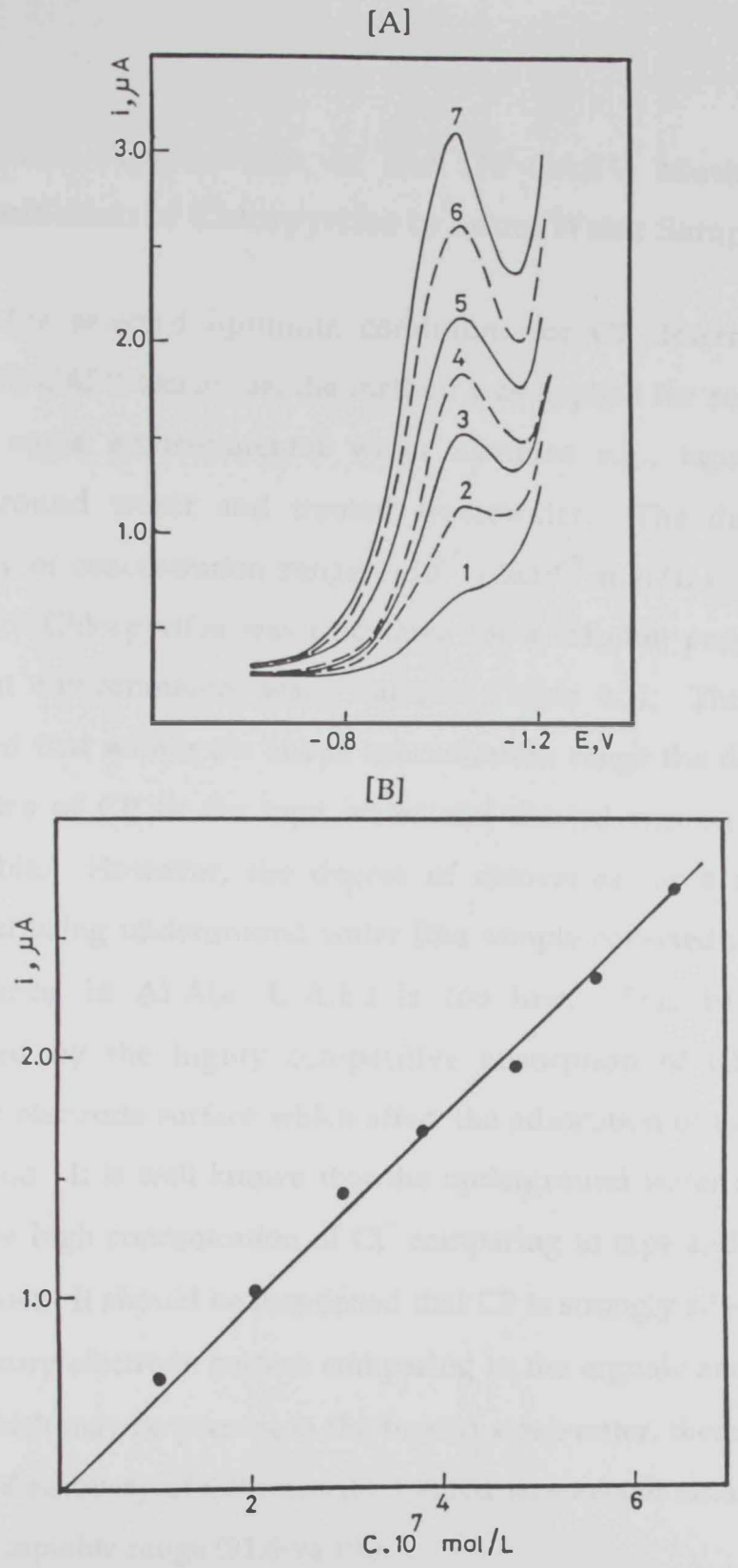


Fig. 4.13. : (A) concentration dependence of the DP-CASV peak of CP at pH 5.01, E_s = -0.4 V, t_s = 180 s and 10 mV/s scan rate. 1) 9.92×10^{-8}, 2) 1.96×10^{-7}, 3) 2.92×10^{-7}, 4) 3.85×10^{-7}, 5) 4.80×10^{-7}, 6) 5.66×10^{-7} and 7) 6.52×10^{-7} mol/L CP.

(B) Calibration curve plot.

4.3. Analytical Application of the DP-CASV Method for Determination of Chlorpyrifos in Some Water Samples

Under the selected optimum conditions for CP determination using DP-CASV technique, the method was applied for analysis of CP in some environmental water samples e.g., tape water, underground water and treated wastewater. The degree of recovery of concentration range $1x10^{-7}$ - $5x10^{-7}$ mol/L (0.034-0.17 mg/L) of Chlorpyrifos was calculated for a solution prepared in different environmental water samples (Table 4.1). The results indicated that within the above concentration range the degree of recoveries of CP in the tape water and treated wastewater are acceptable. However, the degree of recoveries for a solution prepared using underground water (the sample collected from Al-Saad farms in Al-Ain, U.A.E.) is too low. This behaviour explained by the highly competitive adsorption of Cl^- at the mercury electrode surface which affect the adsorption of the tested compound. It is well known that the underground water contains a relative high concentration of Cl^- comparing to tape and treated wastewater. It should be mentioned that CP is strongly adsorbed at the mercury electrode surface comparing to the organic and humic acids which may be present in the treated wastewater, therefore the degree of recovery of CP from the treated wastewater solution are in the acceptable range (91.6-94.1%).

Table 4.1. : Degree of recoveries of CP prepared in various environmental water samples.

Water type	Concentration range		Recovery % (n = 5)
	mol/L	mg/L	
Tape water	$1x10^{-7}$ - $5x10^{-7}$	0.034 - 0.170	96.6 - 103.4
Treated wastewater	$1x10^{-7}$ - $5x10^{-7}$	0.034 - 0.170	91.6 - 94.1
Underground water	$1x10^{-7}$ - $8x10^{-7}$	0.068 - 0.272	76.3 - 83.5

4.4. Detection and Semiquantitative Determination of Chlorpyrifos in Tomato Plant

The chlorpyrifos compound was extracted from tomato tissue using n-hexane (procedure of extraction P. 46). The n-hexane extract was evaporated and the solid residue was dissolved in buffer solution of pH 5.01 containing 25% ethanol and 0.025 M $NaNO_3$. 10 mL of the solution was placed in the voltammetric cell and under the optimum conditions for CP determination it gives a DP-CASV peak at -1.28 V. This peak corresponding to the cathodic reduction peak of CP. The CP concentration in the solution was determined using multi-step standard addition method (Fig. 4.14). After addition of standard solution of CP to the volummetric cell the peak was growth within the same potential range confirming that the original peak is the cathodic reduction peak of CP extracted from tomato plant. From the standard addition calculation, it was found that the concentration of the extracted CP from tomato tissue is 2.66×10^{-7} mol/L (0.091 mg/L). This result indicates that the concentration of CP in tomato tissue is 0.0182 mg CP/Kg tomato.

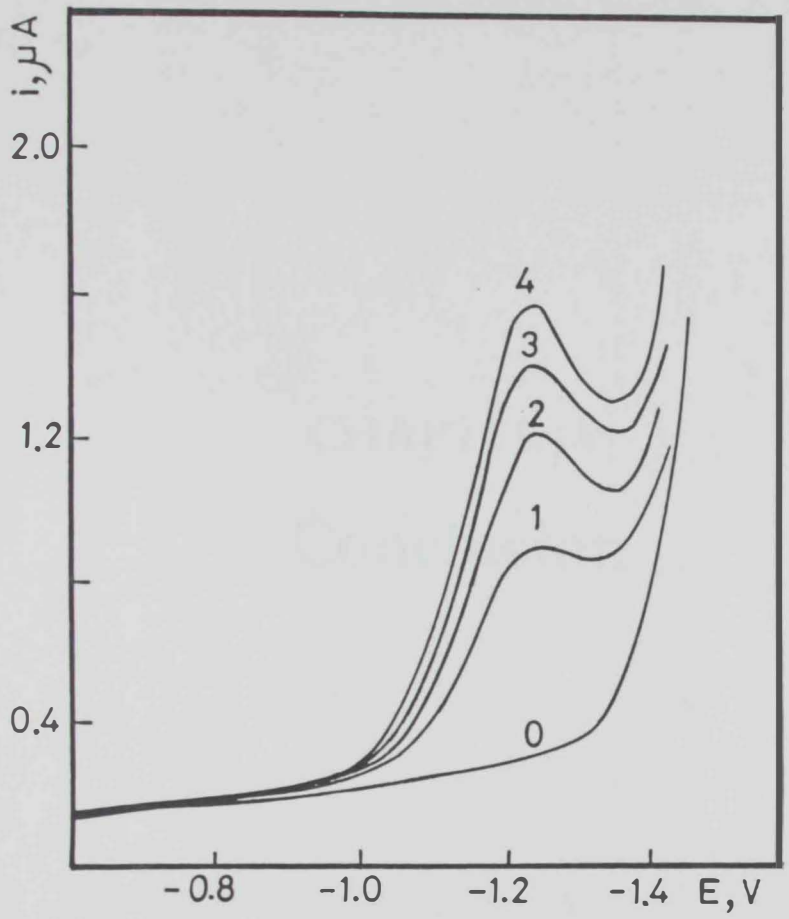


Fig. 4.14. : Application of the standard addition method for determination of the CP extracted from tomato plant.

0) blank solution, 1) 10 mL of the extracted CP , 2) 9.98×10^{-8} , 3) 1.96×10^{-7} , 4) 2.91×10^{-7} mol/L CP.

CHAPTER V

Conclusion

5. Conclusion

Polarography and voltammetry have been widely applied for determination and trace analysis of inserting organic compound, e.g. pesticides. The analysis process proceeds either directly for the organic molecules containing electroactive group, e.g. $\rangle C = N$ or indirectly by analysis of their metal in complex and charge transfer complex.

Chlorpyrifos compound containing an electroactive $\rangle C = N$ group which is reduced to $\rangle CH - NH -$ via $2e^- / 2H^+$ mechanism. Therefore, the investigated compound displays a well-defined reduction peak at the mercury electrode. The concentration dependence of this peak was employed for determination and trace analysis of Chlorpyrifos using DPP and CAS-DP techniques.

The peak height dependence of the differential pulse polarographic reduction peak of CP on the various solutions and the operational conditions was carefully examined. The most sensitive peak was recorded at pH 2.2 in presence of 0.025 M $NaNO_3$ and 25% ethanol. In addition to the latter solution conditions the operational conditions which were selected as optimum conditions for CP determination are 50 mV pulse amplitude, 2 mV/s scan rate, 1.4 s drop time and 22 °C. Under these optimum conditions CP was determined using DPP down to 6×10^{-7} mol/L.

DPP could be applied for the determination of CP compound in various environmental water types, e.g. tape, treated- and

underground-water. However, we can not use the DPP technique for trace determination of CP in plant tissue because its concentration level is too low.

Adsorption and accumulation of the organic compounds at the charged mercury electrode surface are considered as prerequisite steps for analysis of the organic compounds using stripping voltammetric techniques. Cyclic voltammetric techniques that is one of the best technique could be used to detect the adsorbability of the organic compounds at the charged mercury electrode surface.

The CV response of the CP compound displays an irreversible cathodic peak located at highly negative potentials corresponding to the $>C=N$ reduction. The CV behaviour of CP under various operational conditions indicates that the oxidized form is strongly adsorbed and accumulated at the mercury electrode surface at potential close to the electrocapillary zero charge of the electrode (-0.4 V).

The DP-CASV behaviour of CP displays a cathodic reduction peak very sensitive to $[CP]/[H^+]$ ratio in acidic solutions. The slightly acidic and neutral the reduction peak is mainly depends on concentration. In order to select the optimum conditions for trace analysis of CP using CASV method the dependence of its reduction peak on the solution and operational conditions was examined. The optimum conditions was found to be pH 5.01, pulse amplitude 50 mV scan rate 10 mV/s, adsorption potential -0.4 V and

accumulation time between 180-240 s. The detection limit was found $1x10^{-8}$ mol/L of CP at 300 s deposition time.

The DP-CASV was applied for the determination of the degree of recovery of CP from tape-water, treated waste water and underground water. Over a range of $1x10^{-7}$ - $5x10^{-7}$ mol/L (0.034-0.17 mg/L) concentration the degree of recoveries of CP from tape- and underground water are in the range of 91.6 - 103.4%. However, the competitive adsorption of Cl^- content in the underground water at the mercury electrode surface leads to decrease the degree of recovery of CP from the underground water to 76.3-83.5%.

The determination of CP in plant tissue, e.g. tomato tissue was studied using solvent extraction technique followed by DP-CASV. It was found that the concentration of the CP extracted from the tomato tissue was $2.66x10^{-7}$ mol/L (0.091 mg/L). Also, the results indicated that CP could be determined in tomato tissue down to 0.0182 mg/CP/Kg tomato. The amount of CP in tomato tissue was determined using a standard addition method.

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Arabic Summary

شديدية على سطح القطب الزئبق . و بناء على ذلك تم استخدام تقنية cathodic striping voltammetry في التقدير الكمي للمركب تحت الظروف المثالية الآتية : رقم هيدروجيني ٥,٠١ سرعة تسجيل ١٠ مل فولت / ث ، جهد امتزاز _ ٠,٤ فولت ، أما زمن الإمتزاز فقد تراوح بين ١٨٠ و ٢٤٠ ثانية تحت هذه الظروف أمكن تقدير المركب إلى مستوى يصل إلى ١ × ١٠ $^{-8}$ مول / لتر كذلك أمكن حساب كفاءة تقدير المركب في عينات مختلفة من المياه و كانت كفاءة التقدير تتراوح ما بين ٩١ ٪ إلى ١٠٣ ٪ إلا أنها كانت أيضا منخفضة نسبيا في المياه الجوفية (من ٧٦٪ إلى ٨١٪) . كذلك أمكن استخلاص المبيد من عينة من نبات الطماطم و تقديره و قد وجد أن تركيز المبيد في أنسجة نبات الطماطم تصل إلى ٠,٠١٨ جزء في المليون في كل كجم من الطماطم .

نستطيع الحكم على أنه يمكن استخدام تقنيات البولاروجرافي و الفولتامتري في التقدير الكمي الدقيق لمبيد الكلوروبيرفوس بالطريقة المباشرة في أوساط بيئية مختلفة .

الجزء التجريبي :

اشتمل هذا الجزء على طرق تحضير المحاليل القياسية المستخدمة في الرسالة بالإضافة إلى طرق تحضير المبيد الذي تمت الدراسة في أوساط مائية مختلفة ، كذلك طريقة استخلاص و تقدير المبيد من عينة من نبات الطماطم .

اشتمل هذا الجزء أيضا على شرح تفصيلي لأنواع الأجهزة المستخدمة في التحليل البولاروجرافي و الفولتامتري و كذلك الخطوات العامة و المثالية لدراسة السلوك الكهروكيميائي لمركب تحت الدراسة على قطب الزئبق النقاط باستخدام بولاروجرافيا النبضة التفاضلية (Differential Pules Polargraphy)

النتائج و المناقشة :

أظهر السلوك البولاروجرافي للمركب أنه يعطي موجة اختزالية واضحة تقابل اختزال مجموعة الآزوميثين (C = N) الخاصة بحلقة البيريدين . و قد تم إيجاد الظروف المثالية التي تعطي أعلى حساسية للموجة الاختزالية .و تحت هذه الظروف أعطت علامة درجة التغير في التركيز مع ارتفاع الموجه منحنى قياسي في صورة خط مستقيم في ضمن المدى ٠,٩٩ × ١٠ $^{-٦}$ إلى ٦,٥٤ × ١٠ $^{-٦}$ ، أمكن استخدام هذا المنحنى في تقدير المبيد الأوساط المائية المختلفة و قد اشتملت الدراسة أيضا على تأثير الكثير من المتداخلات مثل أيونات الفلزات و الأنيونات و بعض المبيدات الأخرى على عملية التقدير . و قد سجلت الدراسة كفاءة عملية التقدير في الأوساط المائية المختلفة حيث أعطت كفاءة بنسبة من ٩٣,٢ ٪ إلى ١٠٤,١ ٪ إلا أن هذه القيم كانت منخفضة نسبيا في حالة المياه الجوفية .

تمت دراسة السلوك الكهروكيميائي للمركب باستخدام Ciclic Voltammetry و ذلك للوقوف على درجة و قوة امتزازية المركب على سطح قطب الزئبق باعتبارها خطوة أساسية في عملية التقدير الفولتامتري و قد أظهرت الدراسة أن الصورة المؤكسدة من المركب لها قوة امتزاز

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الملخص العربي

مقـــدمـــة :

من أساسيات العمل في مجال حماية البيئة و التلوث هو التعرف المباشر على مدى التلوث و قياسه في الأوساط البيئية المحيطة بنا ، و يعتمد هذا إلى حد كبير على نتائج التحاليل البيئية المختلفة ، و لذلك أصبح من المهم تطوير تقنيات التحاليل الكيميائية المختلفة بهدف العمل على متابعة درجة التلوث البيئي بالمواد العضوية و الغير عضوية ، يعتبر مركب الكلوربيرفوس (دورسبان) من أحد فصائل المبيدات العضو فسفورية و تستخدم بفعالية و على مدى واسع في مجال مقاومة الآفات في مجال الزراعة .

طبقت طرق تحليلية عديدة في التقدير الكمي و التحاليل الدقيقة لكثير من المبيدات العضوفسفورية فمثلا استخدمت طرق التحليل الطيفي ، و التحليل الطيفي الكيناتيكي و الأنواع المختلفة من التحليل الكروماتوغرافي في لتحليل العديد من المبيدات كذلك متابعة نواتج التكسر البيولوجي و الأنزيمي للمبيدات .

يعتبر التحليل البولاروجرافي و الفولتامتري من أدق أنواع التحاليل الكهروكيميائية في مجال تحليل المبيدات خاصة منها تلك التي تحتوي على مجموعة نشطة كهربيا ، حيث أننا نستطيع أن نصل إلى مستوى تقدير يصل إلى ١ × ١٠ $^{-٩}$ مول / لتر تقريبا ، و لذلك احتوت هذه الرسالة على تطبيق تقنيات البولاروجرافي و الفولتامتري في التقدير الكمي الدقيق الكلوربيرفوس بطرق مختلفة و كذلك في أوساط بيئية مختلفة .

و يتضمن الباب الأول للرسالة مقدمة عن المردود البيئي لاستخدام أنواع المبيدات المختلفة في مجال الزراعة بالإضافة إلى تسجيل للأبحاث السابقة التي أجريت على التقدير الكمي للعديد من المبيدات العضوفسفورية .

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اسم الطالب: علي سعيد راشد المقبالي

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السلوك البولاروجرافي والفلتامتري للكلوربيرفوس وتقـديـره فـي بعـض عينـات المـــاء والنبـــات

رسالة مقدمة من الطالب
علي سعيد راشد المقبالي
بكالوريوس في العلوم (رئيسي كيمياء /فرعي جيولوجيا)
كلية العلوم ـ جامعة الامارات العربية المتحـدة (١٩٨٩)

استكمالا" لمتطلبات الحصول على درجة الماجستير في العلوم
(علـــوم البيئـــة)

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