Arylacopyrazoline-5-ones and the related heterocycles are extensively used in pharmaceutical and dye stuff industries. The azo compounds also offer several advantages in the polarographic determination of non-electroactive metals. It is therefore interesting to know their redox (chemical and electrochemical) behaviour. It is difficult to predict this behaviour because of the adsorption of azo compounds at the electrode interface.

Aromatic azo compounds undergo 2-electron reduction at the dropping mercury electrode to hydrazo stage. However, in presence of electron donating groups such as \( -\text{NH}_2 \), \(-\text{OH}\), the reduction proceeds via a 4-electron step to the amine stage. The azo (\(-\text{N-N-}\)) group is expected to undergo cleavage at \(-\text{N-N-}\) single bond depending on the experimental conditions and the structural features of the molecule in which the group is presented.

In view of the paucity of the information on the electro-chemical behaviour of these compounds, the author has taken up the polarographic and cyclic voltammetric studies on 1-phenyl-3-amino-4-arylacopyrazoline-5-ones.
and its arylazo substituted compounds in the pH range 2-10 and in solutions of HCl and NaOH.

The compounds investigated include:

1. 1-Phenyl-3-amino-4-aryazo pyrazoline-5-one
2. 1-Phenyl-3-amino-4-(4'-methylbenzeneazo)pyrazoline-5-one
3. 1-Phenyl-3-amino-4-(2'-methylbenzeneazo)pyrazoline-5-one
4. 1-Phenyl-3-amino-4-(4'-methoxybenzeneazo)pyrazoline-5-one
5. 1-Phenyl-3-amino-4-(2'-methoxybenzeneazo)pyrazoline-5-one
6. 1-Phenyl-3-amino-4-(4'-chlorobenzeneazo)pyrazoline-5-one
7. 1-Phenyl-3-amino-4-(2'-chlorobenzeneazo)pyrazoline-5-one
8. 1-Phenyl-3-amino-4-(4'-nitrobenzeneazo)pyrazoline-5-one
9. 1-Phenyl-3-amino-4-(2'-nitrobenzeneazo)pyrazoline-5-one
10. Arylhydrazones of cyanoaceticester
11. para Nitro arylhydrazones of cyanoaceticester
12. ortho Nitro arylhydrazones of cyanoaceticester

The results are presented in this thesis.

The thesis is divided into three parts.

PART I General Introduction
PART II Experimental
PART III Polarographic and Cyclic voltammetric behaviour of arylazo-pyrazoline-5-ones.

Part I consists of Chapters 1 and 2. Chapter 1 summarizes the information available in the literature
on the electro-chemical behaviour of the azo group (-N=N-) under different experimental conditions. A brief survey of the earlier work reported in the literature on the polarographic behaviour of arylazo substituted compounds is presented in Chapter 2.

Part II contains three sections in a single chapter and describes the experimental aspects in Section (i) gives an account of the preparation of arylazo pyrazoline-5-ones. Section (ii) describes the preparation of solutions and other reagents. The description of the salient features of the instruments employed is presented in Section (iii).

Part III consists of Chapters 4, 5 and 6 and describes the results obtained in the polarographic and cyclic voltammetric studies of arylazo pyrazoline-5-ones investigated.

Chapter 4 consists of eleven sections and contains the results on the polarographic reduction of arylazo pyrazoline-5-ones.

Sections (i) and (ii) of Chapter 4 contain the objectives of the investigations and the list of compounds studied and the general experimental procedures adopted.
It is observed that 1-phenyl-3-amino-pyrazoline-5-ones fails to exhibit reduction wave under the experimental conditions, while the azo substituted compounds exhibit reduction waves. The waves that are observed for 1-phenyl-3-amino-4-arylazo pyrazoline-5-ones and its arylazo substituted compounds are attributed to the reduction of exocyclic azo group. All the compounds investigated exhibit a single wave in acidic solutions and two waves in alkaline solutions. The wave observed in acidic solution is irreversible and diffusion controlled. The irreversible nature is attributed to the presence of the bulky group attached to -N=N- linkage. Comparison of the height of the wave with that obtained for simple azobenzene recorded under identical conditions reveals that the number of electrons involved in the wave obtained in the acid pHs is four.

The following mechanism is proposed for the process. The arylazo-pyrazoline-5-one is protonated to yield the hydrazone form. The weak (=N=N-) single bond of the hydrazone is then cleaved with the uptake of two electrons and two protons. The unstable intermediate - A (imine) produced in the above process is then reduced further to yield the amine in a two electron process. The reduction
of the above mentioned two steps occurs at the same potential.

The half-wave potentials shift towards positive value and wave heights increase with increase in the HCl concentration from 0.2 to 1.0 M.

In alkaline solutions, two waves are noticed. The height of the first wave decreases and that of the second wave increases with rise in NaOH concentration in the range 0.2 to 1.0 M. In alkaline medium arylazo compounds exist in the azomethine anionic form and this anionic form is susceptible to chemical cleavage partially in alkaline solutions to the carbonyl compound. The waves observed are therefore ascribed to

(1) the reduction of anion (First wave) and
(2) the reduction of carbonyl compound (Second wave).

The nitro substituted arylazo-pyrazoline-5-ones exhibit an additional wave. The position of the wave on the potential axis shows that this wave is due to the reduction of nitro group.

The half-wave potential of the waves shifts to more negative potential with increase in the size of the cation of the supporting electrolyte. The change in the
concentration of the supporting electrolyte on the other hand has no effect on the half-wave potential. The results pertaining to the effect of organic co-solvent and surfactant on the half-wave potential are explained in terms of electrode reaction mechanism. Increase in the surfactant concentration at pH 4.0 beyond the concentration just sufficient to eliminate the maximum, shifts the half-wave potential to more negative values. Wave heights decrease with increase in the surfactant concentration.

Aryl hydrazones of cyanoacetic ester exhibit a single wave in the pH range 2 - 10. The wave on the potential axis indicates that this wave is due to the 4-electron reduction of -NH-N=C- group.

Chapter 5 describes the effect of substituent on the polarographic behaviour of these pyrazoline-5-ones. Linear plots are obtained for $E_{1/2} - \sigma$ or $E_{1/2} - \sigma^+$ correlations. The $\rho$ values are negative in acid pHs and unbuffered solutions. They however are positive in alkaline solutions. The observed negative $\rho$ value suggests that, not only electron addition but also the electrophilic attack by proton is involved in the reduction process. The $\rho$ values increase with increase in the size of the cation in 0.1 M HCl solutions.
Results obtained in the cyclic voltammetric studies are described in Chapter 6.

It is observed in cyclic voltammetric studies that except in NaOH solutions, the number of peaks in the voltammograms is more than the number of polarographic waves observed for any compound. Except in 1-phenyl-3-amino-4-(2'-nitrobenzeneazo)pyrazoline-5-ones, none of the compounds exhibits any peak in the anodic sweep. The extra peak that is observed in the cyclic voltammetric studies is attributed to the reduction of intermediate imine. Inverted peak (a cathodic peak in the anodic sweep) is observed in solutions of pH 5.1, pH 8.1 and 0.1 M HCl solutions. The inverted peak is attributed to the movement of mercury electrode surface due to the uneven drop polarization. A linear plot is obtained between the cathodic peak potential and $\sigma$. The slope ($P$) of the linear plots is positive and represents the nucleophilic addition of electron. The positive $P$ value suggests that the contribution by electrophilic protonation is negligible in cyclic voltammetric studies.