INTRODUCTION

A short statement outlining the main theme of the publications and the overall contribution this thesis hopes to make to the advancement of knowledge.

In the 1970s we had reported, for the first time ever, mixed-ligand complex formation involving hydroxamic Acids\(^1\) (Appendix I) and had identified linear free energy relationships\(^2\) (Appendix II) between the basicities of hydroxamic acids and the thermodynamic stabilities of mixed ligand complexes of the type ML'L" (M = Cu\(^{2+}\), L' = 8 - hydroxyquinoline-5-sulfonic acid, L" = benzohydroxamic acid or one of its or methyl, methoxy, nitro, or halo derivatives). We had later extended this work to a large number or metal ions, hydroxamic acid derivatives, and different types of other ligands\(^3-9\). The general findings were: a) mixed ligand or 'ternary' complexes involving hydroxamic acids and other ligands, especially the ones having -N, -N or -N, -O donor sites, are thermodynamically favoured over the corresponding metal:ligand::1:2 binary complexes; b) the wavelengths of maximum light absorption (\(^\lambda\text{max}\)) of mixed ligand complexes of several metal ions with hydroxamic acids are generally higher than the \(^\lambda\text{max}\) of the 'parent' binary complexes.
In another sequence of past work\textsuperscript{10-15} we had tried to synthesise such derivatives of N-phenylbenzohydroxamic acid (PBHA) which could be used to chelate certain metal ions and be employed for the later's spectrophotometric microdetermination with better sensitivity and selectivity than achievable with PBHA.

This thesis presents a series of analytical methods which have resulted from the fusion of the two approaches mentioned above and a synthesis of the respective findings. We prepared a new family of reagents, N-phenyl-2-furylacrylohydroxamic acid and its analogs (Figure 1), and formed their mixed ligand complexes with several metal ions, pyridylazo reagents such as PAN (with -N, -O donar sites) serving as the other ligands. For germanium, iron (III), and manganese we used phenylfluorone, tributylphosphate, and trioctylmethyl ammonium cation respectively as the second ligand. The resulting ternary complexes were, as expected from the earlier physicochemical studies, more thermodynamically favoured than the 'parent' binary complexes and were also more sensitive spectrophotometrically. Thus, 'positive synergism' resulted from their conjunctive use. The systems proved to be ideal for highly sensitive analysis of several metal ions. The selectivity of the analytical methods
\[ X = \text{meta or para } H, \text{CH}_3, \text{OCH}_3, \text{Cl}, \text{Br}, \text{I}, \text{NO}_2 \]

**Figure 1**
was enhanced by extracting the metal ions with chloroform or MIBK (methyl isobutyl ketone) solutions of hydroxamic acids prior to molecular or atomic absorption spectrophotometry. Whereas chloroform generally proved suitable in molecular absorption spectrophotometry, the MIBK extracts often turned out to be ideal for atomic absorption spectrometric determinations; the organic extract providing better nebulisation of the metal ions than the later's aqueous solutions, and separations prior to determination adding to selectivity.

The findings have been published mainly in two journals - International Journal of Environmental Analytical Chemistry (published by Gordon & Breach, from UK), and Analytical Letters (brought out by Marcel Dekker, from USA). A list of papers, which form the main body of the thesis, is enclosed. These papers have undersigned as the sole author. The first two references cited in this introduction would feature as appendices in the thesis.

We began the studies with nine new hydroxamic acids\textsuperscript{16-20} but gradually added four more to the repertoir as the studies progressed.

We hope that the new methods presented in this thesis contribute substantially to our knowledge and capability \textit{vis a vis} environmental analysis.
References


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