

FOREWARD

The present thesis submitted for the doctor of philosophy (Science) of the University of North Bengal, deals with "Extractive-Photometric, Gravimetric and Characteristic studies on Complexes of Some Heavy Metals." The work has been done by the candidate at the Department of Chemistry, University of North Bengal. Portions of the work appearing in parts I, II, III have already been published in 1. Indian Journal of Chemistry, 1982, 21A, 857-58, 2. Indian Journal of Chemistry, 1983, Jan. issue. 3. Current Science (in press) which deals with extractive-photometric determination of copper and palladium, and gravimetric determination of palladium with acenaphthenequinonedioxime and studies of some properties of the dioxime complex.

The thesis is divided into three parts and opens with two general introduction - one to liquid-liquid extraction using mixed ligands and the other to gravimetric determination of metals. Part I and Part II are divided into some other sub-sections. In every sub-section a brief review of the different methods is given followed by experimental details of the work, results and discussion.

Reference cited in the thesis have taken from original or translated papers, reviews and sometimes from text-books on chemical abstracts.

Part-I

Section 1 : Copper forms green coloured complexes in α -picoline/ β -picoline/ γ -picoline/ 2:4:6-collidine-thiocyanate system at pH 3-8. These are extractable into chloroform. The colour of the extract (stable at least for 24 hr) can be directly measured spectrophotometrically. The results are fairly precise and reproducible. Effect of pH, reagent concentration, interference of some diverse ions on the extraction behaviour are tested. The method has been applied in the determination of alloys.

Section 2 : Cobalt forms complexes with α -pic./ β -pic./ γ -pic./ 2:4:6-collidine-thiocyanate system. These complexes are readily extractable into ethyl acetate. All species absorb sharply at 620 nm. The colour of the extracts are extremely stable and can be directly measured spectrophotometrically. The results are fairly precise and reproducible. Effect of pH, reagent concentration, interference of some diverse ions on the extraction behaviour are tested. A quick and very simple method has been proposed for determination of microgram amounts of Cobalt in presence of copper and iron.

Section 3 : Palladium forms complexes with pyridine/ α -pic./ β -pic./ γ -pic./2:4:6-collidine in the presence of thiocyanate. These complexes are quantitatively extracted into chloroform and thus provide

a method for the estimation of Pd(II). All the species absorb around 310 nm. The results are fairly precise and reproducible. Effect of pH, reagent concentration, diverse ions etc have been studied.

Section 4 : "Extractive-gravimetric determination of Ni(II) and its separation from binary mixtures using pyridine and substituted pyridines in thiocyanate system" — Ni(II) forms sky blue chloroform soluble complexes with pyridine/ β -pic./ γ -pic. - thiocyanate system but it fails to do the same when the methyl group is in the 2- position of the pyridine ring. Separation of Ni(II) from binary mixtures containing Co(II), Cu(II) and Pd(II) has been described. The method is fairly precise and reproducible. Effect of pH, reagent concentration, diverse ions etc. have been examined.

Part-II

Section 1 : Synthesis of acenaphthenequinonedioxime from acenaphthene has been described.

Section 2 : Ni(II) precipitates quantitatively by acenaphthenequinonedioxime (ANDO) within the pH range 6.8 - 8.4. After drying the precipitate at 110° , its composition corresponds to the formula $Ni(C_{12}H_7O_2N_2)_2$. ANDO has been used as a reagent for gravimetric determination of Ni and for its separation from commonly associated cations and anions. Many commonly associated ions, except Fe(III),

Co(II) and Cu(II) do not interfere. Solvent-extraction techniques have been utilized to separate Cu(II) and Co(II) from binary mixture. For masking Fe(III) excess citrate ions has been used. The results are fairly precise and reproducible. The effect of pH, diverse ions and the range suitable for sensible estimation, and finally the effect of excess-reagent have been studied.

Section 3 : Ni(II) forms water insoluble mixed complex with ANDO and dimethylglyoxime (DMG) quantitatively within the pH range 6.2-8.8. The complex having the composition 1:1:1 (Ni:ANDO:DMG) can be dried to a constant weight at 105-110°C. Interference due to Fe(III) is removed by an excess citrate ions. Co(II) and Cu(II) are removed by solvent-extraction as 2-substituted pyridine-thiocyanate complex. The results are fairly precise and reproducible. The effect of pH, reagent concentration, diverse ions etc. have been studied.

Section 4 : ANDO has been used as a gravimetric reagent for Pd(II). Pd(II) quantitatively precipitates by ANDO between the pH range 0.5-3.5. After drying the precipitate at 110°C, its composition corresponds to the formula $\text{Pd}(\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}_2)_2$. Many commonly associated ions, except Pt(IV) and Fe(III) do not interfere. Interference due to Fe(III) has been eliminated by masking it with excess citrate ions. The results are fairly precise and reproducible. The effect of pH, reagent concentration, diverse ions and the range suitable

for sensible estimation have been studied.

Section 5 : Pd forms mixed dioxime complex with ANDO and DMG quantitatively within the pH range 0.7-3.8. The complex having the composition 1:1:1 (Pd:ANDO:DMG) can be dried to a constant weight at 105-110°C. Interference due to Fe(III) has been removed by an excess of citrate ions. Based on precipitation in different pH solutions, gravimetric determination of Pd(II) and Ni(II) in their binary mixture has been carried out with satisfactory results. The results are fairly precise and reproducible. The effect of pH, diverse ions, the range suitable for sensible estimation etc have been studied.

Section 6 : Copper precipitates by ANDO quantitatively within the pH range 4.6-7.2. This reagent has been utilized for gravimetric estimation of copper in milligram level. After drying the precipitate its composition corresponds to the formula $\text{Cu}(\text{C}_{12}\text{H}_7\text{O}_2\text{N}_2)_2$. The effect of pH, diverse ions, excess reagent have been studied, and also the optimum condition for quantitative precipitation has been established. The results are fairly precise and reproducible.

Section 7 : ANDO has been used as a reagent for gravimetric determination of Cobalt and for its separation from several cations and anions. Cobalt is quantitatively precipitated by ANDO between the pH range 4.57-7.02. After drying the precipitate at 110°C, its

composition corresponds to the formula $\text{Co}(\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}_2)_2$. The results are fairly precise and reproducible. The effect of pH, reagent concentration, the range suitable for sensible estimation etc. have been studied, and the optimum condition for quantitative estimation has been established.

Part-III

In this part the properties of the dioxime complexes, such as $\text{Ni}(\text{ANDO})_2$, $\text{Ni}[\text{ANDO}(\text{DMG})]_2$, $\text{Cu}(\text{ANDO})_2$, $\text{Co}(\text{ANDO})_2$, $\text{Pd}(\text{ANDO})_2$ and $\text{Pd}[\text{ANDO}(\text{DMG})]_2$ have been studied. By elemental analysis, magnetic susceptibility measurement, infrared and far infrared spectra, ultraviolet and visible spectra, thermogravimetric analysis and differential thermal analysis square planar geometry of the metal chelates have been proposed.