

Synopsis of the dissertation entitled, "Photometric determination of some transition metals with mercaptopyrimidines" submitted by Smt. R.D. Wagh for the M.Phil. degree in Chemistry to Shivaji University, Kolhapur-4.

The present investigation embodies the results of intensive studies on the use of 1-(2'-chlorophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol (2'-chloro PTPT) as spectrophotometric reagent for copper(II). It also includes the use of 1-(4'-bromophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol (4'-bromo PTPT) as analytical reagent in the solvent extraction separation of Gold(III) and extraction spectrophotometric determination of Rhodium(III). The dissertation consists of five chapters.

Chapter I

In this chapter the theory of spectrophotometry is given covering the laws of absorption, limitation to applicability of Beer's law etc.

Chapter II

The chapter second gives an account of synthesis and characterisation of

- (i) 1-(2'-chlorophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol and

(ii) 1-(4'-bromophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol.

The broad review of mercaptopyrimidines reported in the literature is also given. The purity of the reagents was checked from their elemental analysis, melting point and spectral characteristics. Further the purity of the pyrimidine-thiols was checked by titrimetric method of analysis with standard solution of sodium methoxide (0.05 M) in benzene-methanol solution by using Azo-violet as an indicator. It was found that the reagents are of 99.6% pure.

Chapter III

This chapter is devoted to describe the systematic studies on synergic solvent extraction of copper (II) with 2'-chloro-PTPT (Pyrimidinethiol I) in combination of neutral base pyridine. In absence of pyridine extraction of copper (II)-pyrimidinethiol I complex commence at pH 5 (in acidic medium) and becomes quantitative at pH 8 (in basic medium), with 8 min shaking. In presence of pyridine however, extraction starts at pH 1.0 and becomes quantitative at pH 4.0. There is also increase in the absorbance by 10% in presence of pyridine. Thus pyridine exerts a synergic effect on the extraction of copper (II)-pyrimidinethiol I complex enabling the rapid and quantitative extraction of copper (II) from acidic medium. The method has been applied for the determination of copper (II) in alloys and drugs.

Chapter IV

The chapter describes the solvent extraction studies of Gold(III) with 4'-bromo-PTPT from acidic medium. A chloroform solution of pyrimidinethiol II extracts the colourless complex of Gold(III) quantitatively in a single extraction in 5-10 sec and Gold(III) is determined with stannous chloride method after destruction of organic matter. The capacity of pyrimidinethiol II for Gold(III) extraction at acidity range 0.5 - 8 M HCl with 10 ml of 0.01 M of reagent in chloroform was 5.5 mg.

Chapter V

The study of spectrophotometric determination of Rhodium (III) using 4'-bromo-PTPT (pyrimidinethiol II) is described in this chapter. Rhodium (III) reacts with 4'-bromo PTPT in hot aqueous solution (10 min heating on water bath) at 2-3 M HCl to form yellow complex extractable into methyl isobutyl ketone (MIBK). The complex is measured at 355 nm against the solvent blank. The system obeys Beer-Lambert's law in the range 2-32 ppm Rh (III) at 355 nm. The molar extinction coefficient of the complex is $2637 \text{ L mol}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity of 39 ng cm^{-2} . The interference study shows that the Rhodium (III) can be determined without interference of many ions and fairly large amount of common anions. The method is simple selective and also reproducible.

Every chapter from 3-5 opens up with a brief but upto-date literature survey of reagents reported for extractive spectrophotometric determination of copper (II), Rhodium (III) and extraction of Gold(III). An attempt has been made to study the methods described critically with regard to sensitivity, accuracy and precision. The proposed ligand appears versatile and promising as an extractant for Gold(III) and extractive spectrophotometric reagent for copper (II) and Rhodium (III).