CHAPTER - II

METHYLTHIENYLKETONE THIOSEMICARBAZONE AS A SPECTROPHOTOMERIC REAGENT FOR RUTHENIUM (III)

CHAPTER - IIA

SYNTHESIS AND CHARACTERISATION OF METHYL THIENYLKETONE THIOSEMICARBAZONE (MTKT)

INTRODUCTION

Thiosemicarbazones are a class of compounds obtained by condensing thiosemicarbazide (TSC) with suitable aldehydes or ketones, these compounds are easily crystallisable and possess sharp melting points. Hence, they have long been commonly used for identification of individual aldehydes and ketones. However, the first report on analytical use of this class of compounds was made by Scott et al. as late as 1945[1]. Since then voluminous work on their analytical applications has appeared in the literature. The realisation of the importance of thiosemicarbazones as analytical reagents is reflected in gradual increase in the number of papers, dealing with their applications in analytical problems. The review of the work on transition metal complexes of thiosemicarbazides and thiosemicarbazones was written by Campbell[2]. Singh[3] et al. recently gave a critical review on analytical applications of thiosemicarbazones and semicarbazones. Thiosemicarbazones contain active grouping for chelation as shown below

$$= N - NH - \underset{\underset{S}{\|}}{C} - N =$$

which involves bonding through sulphur atom with possible

further coordination by the hydrazine nitrogen atom to give a five membered chelate ring. Depending upon the type of aldehyde or ketone used for condensation, thiosemicarbazones can act as unidentate, bidentate or multidentate chelating agents for several metal ions producing highly coloured complexes. In case of unidentate ligands, bonding occurs only through the sulphur atom. The coloured complexes are used in selective and sensitive determination of metal ions. Domgk[4] et al. pioneered the pharmaceutical applications of metal thiosemicarbazone for the treatment of tuberculosis. Since then a number of papers have appeared on the pharmacology of these compounds. However these compounds have been shown to be active against influenza[5], protezoa[6], smallpox [7] and certain kinds of tumours[8] and possess very good pesticidal[9] and fungicidal[10] activity. The biological activity of thiosemicarbazones may be attributed to the ability of the reagent to form chelates with traces of metal ions present in biological systems. The antituber activity of p - acetamidobenzaldehyde thiosemicarbazone is found to be enhanced by the presence of small amounts of copper ions[11]. These findings have led recently to an increased interest in the chemistry of transion metal chelates of thiosemicarbazones.

A large number of thiosemicarbazones are used as spectrophotometric reagents in analytical chemistry. They are used for trace determination of metal ions in various materials. Metal -

thiosemicarbazone complexes are formed in conditions ranging from moderately acidic to moderately alkaline. However, there are relatively few reports on spectrophotometric determination of metal ions in highly acidic medium [12-14]. Metal complexes are also extractable in various organic solvents resulting in an enhanced sensitivity thereby enabling extraction and simultaneous photometeric determination of metal ions [15 - 16]. It was generally observed that thiosemicarbazones containing hydroxy groups ortho to the aldehyde group gave good colour reactions. Besides the applications in spectrophotometry, thiosemicarbazones have been reported as gravimetric reagents for many metal ions [17-20], as indicators in the direct titration of metals with EDTA [21-22], in titration in nonaqueous solvents [23]. Recently reports have appeared on separation of metal ions using thiosemicarbazones by thin layer chromatography on alumina with ethylacetate as solvent [24].

In this chapter the synthesis and characterisation of methyl thienylketone thiosemicarbazone (MTKT) is described.

SYNTHESIS AND CHARACTERISATION OF METHYL THIENYLKETIONE THIOSEMICARBAZONE :

Methyl thienylketone 2g. (10 mM) was dissolved in 20 ml of ethanol and 1 g.(10 mM) of thiosemicarbazide in 20 ml of hot distilled water. The solutions were mixed, 2-3 drops of anhydrous acetic acid were added, and the mixture was refluxed for 2 hours. Then the mixture was cooled to 0^{o}c and the white

crystals obtained were recrystallised from hot (1:1) ethanol water (M.P. 135°C.).

Formula of the compound is $C_7 H_9 S_2 N_3$

	C	H	N	S
Found %	42.10	4.60	32.30	20.95
Calculated %	42.21	4.52	32.16	21.10

for $C_7 H_9 S_2 N_3$

Properties of the reagent :

MTKT ($C_7 H_9 S_2 N_3$ Mol wt. 199.0)

consists of yellow shining crystals, M.P. 135°C. It is sparingly soluble in cold water (0.42 g $liter^{-1}$ at 27°c) but it dissolves in ethyl alcohol, methyl alcohol and chloroform. The organic solvents in which MTKT is sparingly soluble are benzene and carbon tetrachloride. It is moderatly soluble in n - butanol. The solution of MTKT is stable towards light and in dry condition, it can be stored for several months without deterioration. It is stable in hydrochloric acid as well as in alkali.

Ultra - Violet absorption spectrum

The absorption spectrum of MTKT in methenol shows a strong absorbance band at 320 nm and a weak band at 260 nm. The reagent does not absorb in the visible region (Fig. 1.1).

MTKT Solution.

0.25 % W/v solution of MTKT was prepared in 1:1 methanol.

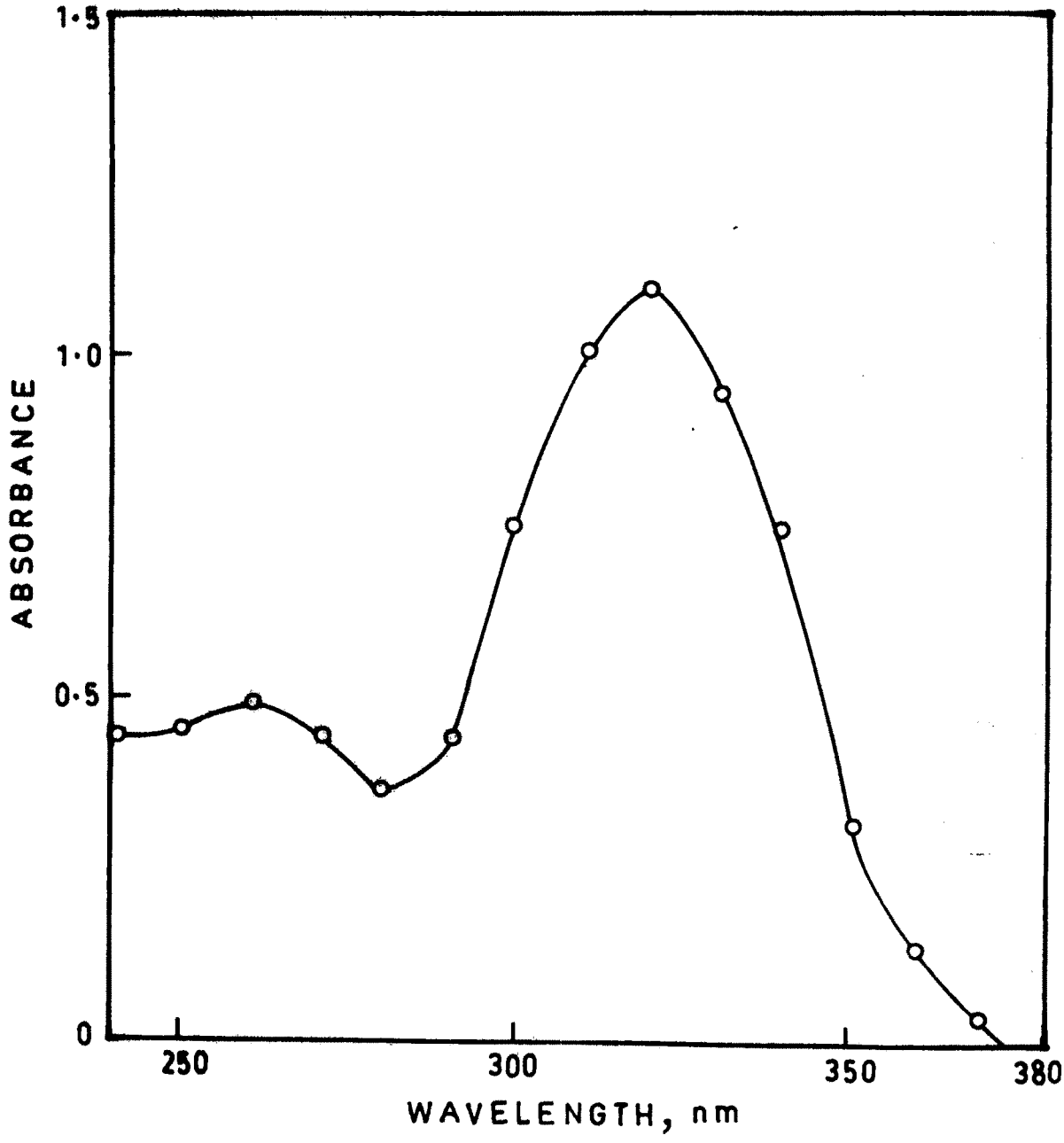

Fig. 2·1 – UV ABSORPTION SPECTRUM OF MTKT IN METHANOL.

ethyl alcohol, methyl alcohol and chloroform. The organic solvents in which MTKT is sparingly soluble are benzene and carbon tetra chloride. ~~It is moderatly soluble~~. It is moderatly soluble in n-butanol. The solution of MTKT in 50 % methenol is stable for at least two months.

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