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**PART - ONE**

**SPECTROPHOTOMETRIC DETERMINATIONS  
OF SOME METAL IONS WITH  
2-ACETYL THIOPHENE GUANYLHYDRAZONE**

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**CHAPTER - I**

***SYNTHESIS AND CHARACTERIZATION OF  
2-ACETYL THIOPHENE GUANYLHYDRAZONE***

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## 1.1 INTRODUCTION

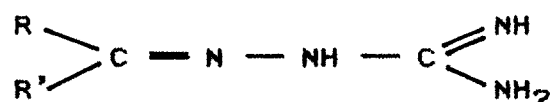
Spectrophotometric methods are preferred for determination of trace amounts of metal ions. These are particularly useful when the insufficient sample is present for the gravimetric and titrimetric methods. Although interference by other metal ions is a serious problem, suitable systems can be developed for the analysis of metal ions in presence of impurities.

The rapid development in science and technology stresses the need for the production of pure materials. Hence the development of new techniques for the determination of trace impurities in highly pure materials is desirable. These techniques have mainly been made in the field of analytical chemistry based on instrumental methods. Spectrophotometry have been used as a routine procedure for trace determinations with adequate accuracy and precision.

Spectrophotometric determinations of inorganic metal ions with organic reagents are based on reactions which yield products absorbing or emitting radiation within the frequency range of electronic spectra. The absorption of UV and visible radiations is thus measured in spectrophotometric applications of organic reagents. The organic reagents find extensive applications in spectrophotometry. The study of organic reagents still attracts many chemists,

because some of these reagents allow development of highly sensitive selective and rapid methods for the analysis of variety of materials.

Schiff's bases have more importance in analytical chemistry. The ligands containing guanidine group offer an immense analytical potentialities. Aldehydes and ketones give easily crystallizable guanylhydrazone derivatives and this property is used for the identification of the compounds with  $\text{>C=O}$  function. Guanylhydrazones react as chelating ligands and form complexes with metal ions. Guanylhydrazones were first synthesised by Thiele and Dralle<sup>1</sup>. Their general structure is



Where R and R' are H or any organic radical. The analytical properties of the guanylhydrazones depend on the structural features of both R and R'. The imine group of the guanylhydrazone can increase the selectivity and sensitivity of the method. 2-Acetyl thiophene guanylhydrazone has been used extensively as an analytical reagent.

Guanylhydrazones are important due to their pharmacological properties.

Several compounds were prepared with guanylhydrazones and are useful as bactericides and insecticides<sup>2-4</sup>, in

treating heart insufficiency and hypersensitivity<sup>5</sup>, in normal leukemia bearing mice as growth inhibitors. Some such compounds have extremely high bacterial activity and are suitable as internal, external and oral disinfectants<sup>6</sup> and are used as antiseptics for food<sup>7</sup>. Several guanylhydrazone complexes have antifungal activity<sup>8</sup> and act as anticancer and antiinflammatory agents<sup>9</sup>. Some compounds possess antileukemic activity, antihistamine activity<sup>10</sup>, antiviral activity<sup>11</sup> and also antimalarial activity.

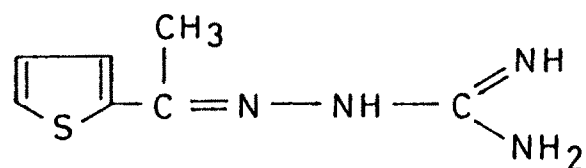
Several steroid guanylhydrazones were prepared<sup>12,13</sup>. Inhibitory effects of these compounds are shown on invitro growth of some dermatophytes. They are also useful in waste water purification, precipitation of organic anions especially dyes from waste water.

Some aminoguanidine derivatives are used in photographic materials and for paper treatment<sup>14</sup>, useful as cationic agents for retention of dyes and pigments on cellulose fibers and provide dry and wet strength in paper. Guanylhydrazone compounds are cardioactive substances<sup>15,16</sup> and are used as new pharmaceuticals<sup>17</sup>

These studies have been very much useful in the chemistry of guanylhydrazone complexes because of the several applications of guanylhydrazone to pharmacology.

The ligand chosen in the present study is 2-acetyl thiophene guanyldrazone (ATG) which exhibits promising analytical properties and hence a detailed investigation was taken up.

This chapter deals with the synthesis and characterization of ATG. The structure of it is



The reagent, ATG is used for the photometric determinations of gold, palladium and iron.

## 1.2 EXPERIMENTAL

### 1.2.1 Apparatus:

The absorbance measurements were done on VIS-Digital spectrophotometer (ELICO MODEL CL-27), equipped with matched pair of glass cuvettes (10.0 mm).

While, absorbance measurements over ultraviolet region were done on UV-VIS -NIR spectrophotometer (HITACHI, Model No-330) equipped with tungsten lamp, red sensitive phototube and photomultiplier. Standard 10.0 mm path length rectangular cells were used.

For pH measurements, Digital pH meter (ELICO, model LI-120) having glass-calomel combination electrode was used. The pH-meter was standardized by using 0.05 M potassium hydrogen phthalate (pH = 4.01) and 0.01 M borax (pH = 9.18) buffers.

All the measurements were done at room temperature ~25° to 30°c

#### 1.2.2 Reagents:

All solvents and reagents were of analytical reagent grade.

Glass distilled conductivity water was used throughout the work.

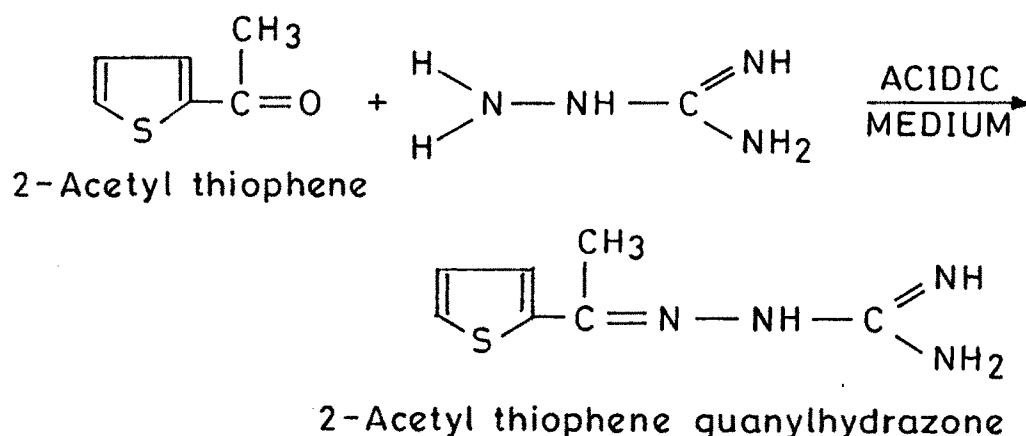
#### 1.2.3 Synthesis of 2-acetyl thiophene guanylhydrazone (ATG):

For the synthesis of 2-acetyl thiophene guanylhydrazone (ATG), aminoguanidine bicarbonate was used instead of aminoguanidine dihydrochloride, which simplifies the synthesis and gave much better yield.

Aminoguanidine bicarbonate 2.0 g was completely dissolved in minimum quantity of concentrated nitric acid (till evolution of carbon dioxide was completely stopped). 2-acetyl thiophene, 1.6 ml was diluted in 10.0 ml ethyl alcohol and both the solutions were mixed together. The

mixture was kept as such overnight. The product was filtered, washed and recrystallised from ethyl alcohol to obtain white shining crystals of 2-acetyl thiophene guanyldiazone (~ 2.0 g.) M.P. = 202°C ± 1°C. The compound is quite stable for months.

The reaction is



#### 1.2.4 Solubility:

The reagent is soluble in hot water, ethanol, dioxane, benzene etc. but insoluble in chloroform and carbon tetrachloride.

The solution of the reagent in 50% ethanol was stable for months without any deterioration.

#### 1.2.5. Characterisation of ATG:

ATG is stable in air. There is no action of light on the reagent. So no special care is required to protect it from light.



The microelemental analysis of the chromatographically purified reagent confirmed the formula to be  $C_7H_{10}N_4S$  (Molecular weight = 182.0 ) The results are given as below.

(ATG)	Carbon	Hydrogen	Nitrogen	Sulphur
Calculated % of elements	46.15	5.50	30.77	17.58
Experimentally found % of elements	46.45	5.65	30.58	17.32

#### 1.2.6. Ultraviolet Spectra of the reagent (ATG):

Figure 1.1 shows the ultraviolet absorption spectra of the reagent (ATG) in 50% ethanol ( $1.0 \times 10^{-3}$  M) at different pH values.

Absorbances and molar extinction coefficients ( $\lambda_{\text{max}}$  260 nm and 320 nm) of the reagent at different pH values are given in table 1.1

Table 1.1 : Spectral characteristics of the reagent (ATG):

pH	Absorbance at $\lambda$		Molar extinction coefficients $\times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	
	260 nm	320 nm	260 nm	320 nm
5.0	1.45	1.02	1.45	1.02
7.0	1.42	1.05	1.42	1.05
9.6	1.40	1.08	1.40	1.08
10.5	1.35	1.15	1.35	1.15
11.9	1.20	1.44	1.20	1.44
12.5	1.10	1.62	1.10	1.62

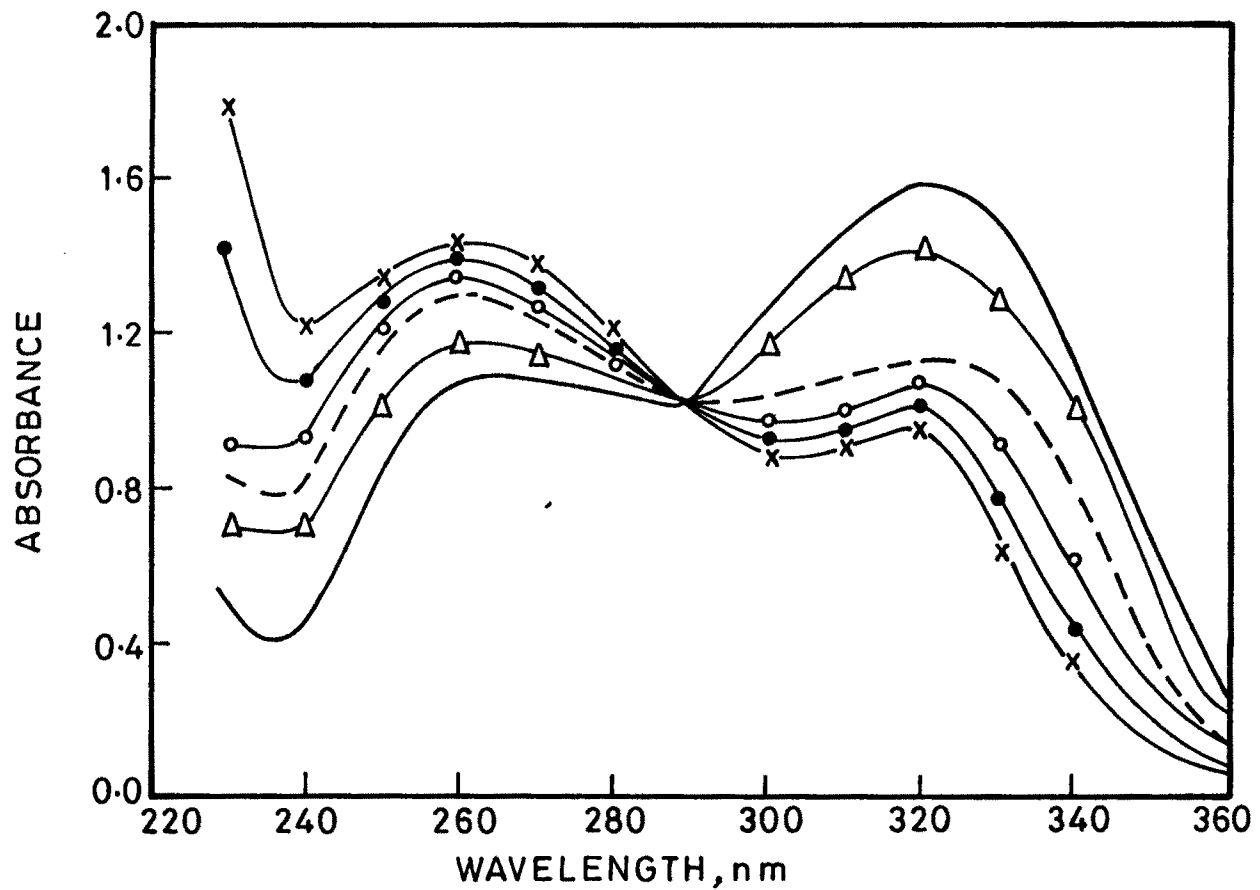


FIG.1.1- ULTRAVIOLET SPECTRA OF REAGENT (ATG)

x—x pH = 5.0      - - - pH = 10.5  
 ●—● pH = 7.0      Δ—Δ pH = 11.9  
 ○—○ pH = 9.6      — pH = 12.5

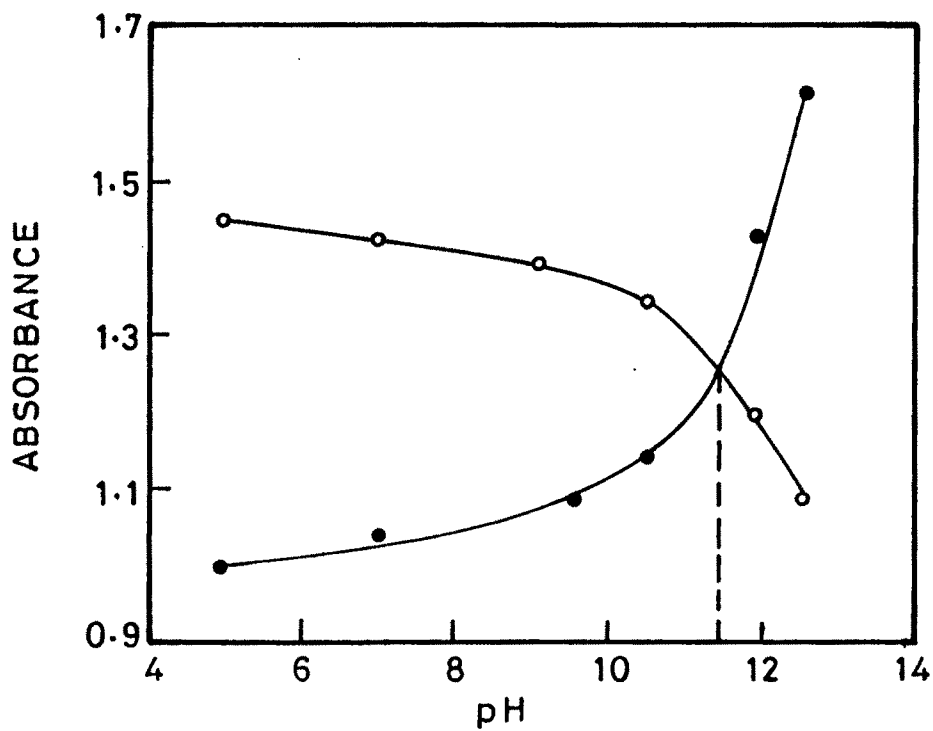


FIG.1.2- DETERMINATION OF pK

○—○ 260 nm ; ●—● 320 nm

### 1.2.7. Infrared Spectrum of the Reagent (ATG):

Infrared absorption spectrum in the range 4000 to 200  $\text{cm}^{-1}$  was run on Perkin Elmer 221 IR spectrophotometer in KBr pellets (Figure 1.3). The characteristic absorption bands were observed as follows:

3460 $\text{cm}^{-1}$	—————>	NH stretch
3200 - 3100 $\text{cm}^{-1}$	—————>	NH <sub>2</sub> stretching
2920 $\text{cm}^{-1}$	—————>	= N - vibrations
2720 $\text{cm}^{-1}$	—————>	} Overtone pattern
2200 $\text{cm}^{-1}$	—————>	
1950 $\text{cm}^{-1}$	—————>	
1890 $\text{cm}^{-1}$	—————>	
1820 $\text{cm}^{-1}$	—————>	
1760 $\text{cm}^{-1}$	—————>	
1680-1600 $\text{cm}^{-1}$	—————>	NH <sub>2</sub> deformation, complicated pattern
1670-1500 $\text{cm}^{-1}$	—————>	N <sub>2</sub> C = N absorption due to guanidine and due to NH deformation and CN stretching vibrations.
1375 $\text{cm}^{-1}$	—————>	CH <sub>3</sub> -C absorption band.
1145, 1050, 820 $\text{cm}^{-1}$	—————>	ortho substitution pattern
770, 725, 710 $\text{cm}^{-1}$	—————>	3 adjacent H wag.
700 - 600 $\text{cm}^{-1}$	—————>	C-S-C linkage.

### 1.2.9. Determination of Ionization Constant of ATG:

The ionization constant of the reagent (ATG) was obtained both by spectrophotometric and pH metric methods.

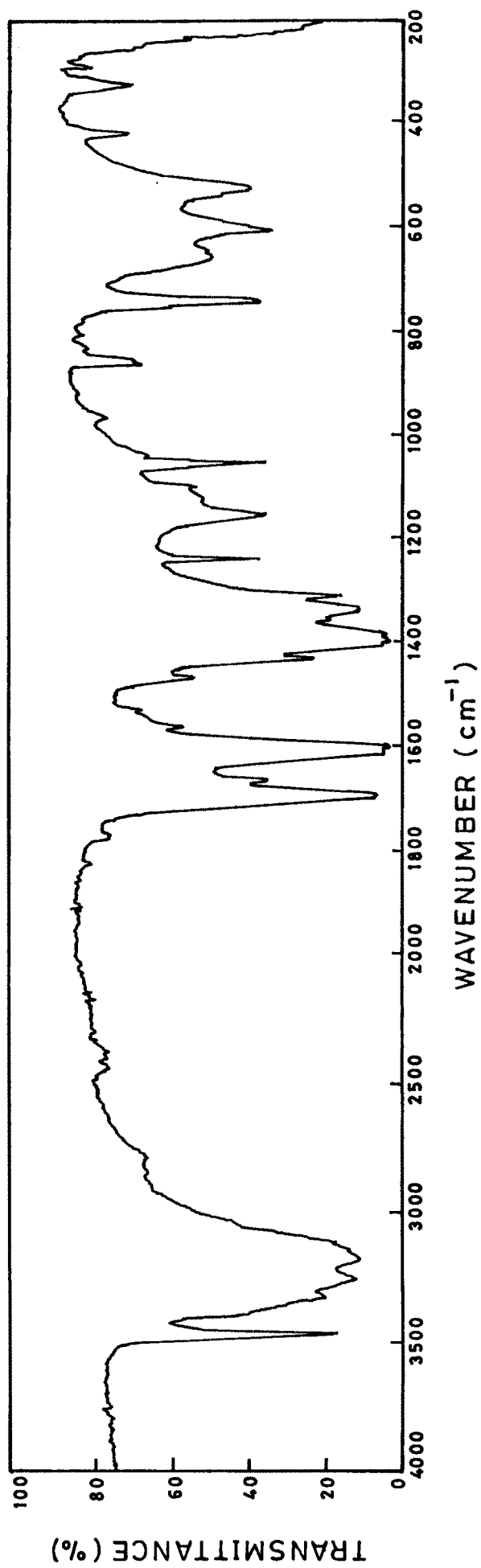


FIG. 1.3 - INFRARED SPECTRUM OF 2-ACETYL THIOPHENE GUANYLHYDRAZONE .

(a) Spectrophotometric method:

Figure 1.1 shows the ultraviolet spectra of the reagent at different pH values. At pH 5.0 the ligand base, L is studied spectrophotometrically which shows the absorption band with  $\lambda_{\text{max}}$  at 260 nm, which lowers in intensity as pH increases. With increasing value of pH, the absorbance at longer wavelength increases, and at pH 12.5, highest intensity band with  $\lambda_{\text{max}}$  at 320 nm appears. All spectral curves pass through the isosbestic point at 290 nm, thereby indicating a dynamic equilibrium between L and its deprotonated species, assuming that at pH 5.0 the molecular form of the ligand is exclusively present and the deprotonated species is absent and that at pH 12.5, the deprotonated species is present exclusively and the molecular form is absent. By using Hinderson equation and also from the half height<sup>18</sup> of the sigmoid curve (Figure 1.2), the pK value for the deprotonation of ligand is found to be 11.45.

(b) pH metric method:

The reagent, ATG 5.0 ml of  $1.0 \times 10^{-2}$  M was taken in a thermostated titration vessel containing 20.0 ml distilled water at  $25 \pm 1^\circ\text{C}$ . The solution was titrated against 0.1 M NaOH. The observations are given in table 1.2. The ionization constants were calculated from the pH values by using the formula.

$$pK = pH + \log \frac{[HA]}{[A^-]}$$

HA represents the reagent, ATG. The  $-\log[H^+]$  values were read from pH meter.

The titration was repeated until two sets of values differing within 0.01 pH units were obtained. The results show that the pK is 11.45 for 2-acetyl thiophene guanyldiazone (ATG).

Table 1.2 : Determination of ionization constant of ATG at  $25 \pm 1^\circ C$   
[ATG] = 0.01 M; NaOH = 0.1 M

NaOH, ml	pH	Stoichiometric concentration		$\log \frac{[HA]}{[A^-]}$	pK
		HA	$A^-$		
0.5	8.97	0.018	0.002	0.954	9.92
1.0	11.00	0.016	0.004	0.602	11.60
1.5	11.48	0.014	0.006	0.367	11.85
2.0	11.70	0.012	0.008	0.176	11.88
2.5	11.85	0.010	0.010	0.000	11.85
3.0	11.95	0.008	0.012	-0.176	11.77
3.5	11.99	0.006	0.014	-0.367	11.62
4.0	12.06	0.004	0.016	-0.602	11.46
4.5	12.12	0.002	0.018	-0.954	11.17
Mean pK =					11.45

#### 1.2.10 Complex Formation:

The reagent, 2-acetyl thiophene guanylhydrazone (ATG) forms complexes with Au(III), Pd(II) and Fe(III). A detailed account of the complex formation with these three metals is discussed in the 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> chapters respectively.

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