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CHAPTER - IV

STUDIES ON METAL TRIAZINE COMPLEXEAS

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## STUDIES ON METAL TRIAZINE COMPLEXES

All the metal complexes prepared namely copper, tungsten, mercury, tin, uranium and thorium triazine (5,6-Diphenyl-2H-[1,2,4]triazine-3-thione) complexes are coloured and stable to air and moisture. The melting points of all the complexes are above 250 °C. and decompose at higher temperature. Complexes are insoluble in water, partially soluble in chloroform and methanol and soluble in coordinating solvents like DMF and DMSO.

### 4.1. Elemental Analysis

The elemental analysis data of complexes is given in Table IV-1. The analytical data of metal, carbon, hydrogen and nitrogen revealed that all the complexes have 1:2 stoichiometry (except thorium having 1:3 stoichiometry). The mass spectral data of complexes is presented in Figures IV-1 to IV-6. The molecular ion peaks for copper (MS m/z, 593.3(M+H)), mercury (MS m/z, 731.3(M+H)), tin (MS m/z, 645.(M-H)) and thorium (MS m/z, 1025.5(M+H)) complexes were coincided with the expected 1:2 (1:3 for thorium) stoichiometry. However molecular ion peaks of tungsten and uranium complexes are not properly resolved due to lower solubility.

Table IV-1: Analytical data of Triazine metal complexes

S.No	Complex	Emperical formula of Complex ion	Colour	Found (Calcd.)%			
				C	H	N	Metal
1	Cu Triazine	$[(C_{15}H_{11}N_3S)_2Cu]$	Brown	58.12 (59.05)	2.94 (3.63)	13.02 (13.77)	10.15 (10.41)
2	W Triazine	$[(C_{15}H_{11}N_3S)_2WO]$	Yellow	49.17 (49.46)	2.04 (2.77)	11.83 (11.54)	23.27 (24.69)
3	Hg Triazine	$[(C_{15}H_{11}N_3S)_2Hg]$	Pale Yellow	50.34 (49.41)	3.54 (2.76)	12.04 (11.52)	28.11 (27.51)
4	Sn Triazine	$[(C_{15}H_{11}N_3S)_2Sn]$	Orange yellow	54.87 (55.66)	2.92 (3.11)	13.13 (12.98)	18.04 (18.34)
5	U Triazine	$[(C_{15}H_{11}N_3S)_2UO_2]$	Orange	46.58 (45.11)	3.14 (2.52)	11.13 (10.52)	--- (29.80)
6	Th Triazine	$[(C_{15}H_{11}N_3S)_3Th]$	Orange yellow	51.14 (52.73)	3.17 (2.95)	11.94 (12.3)	--- (22.64)

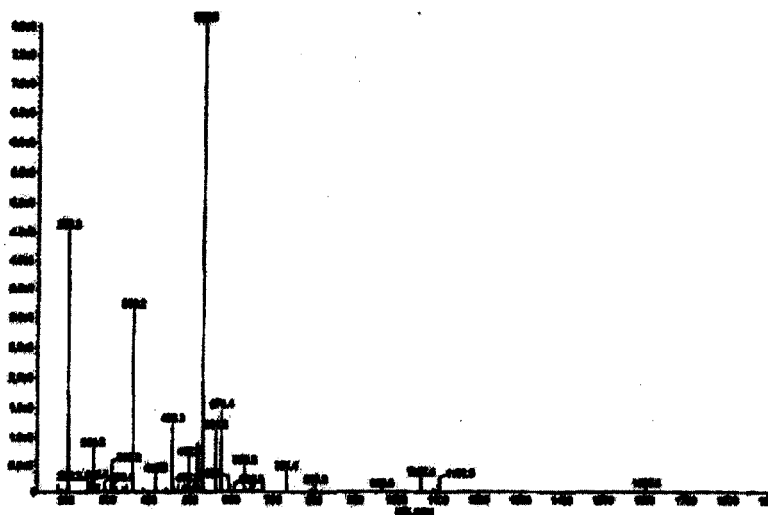


Figure IV - 1: Mass spectra of Cu-Triazine

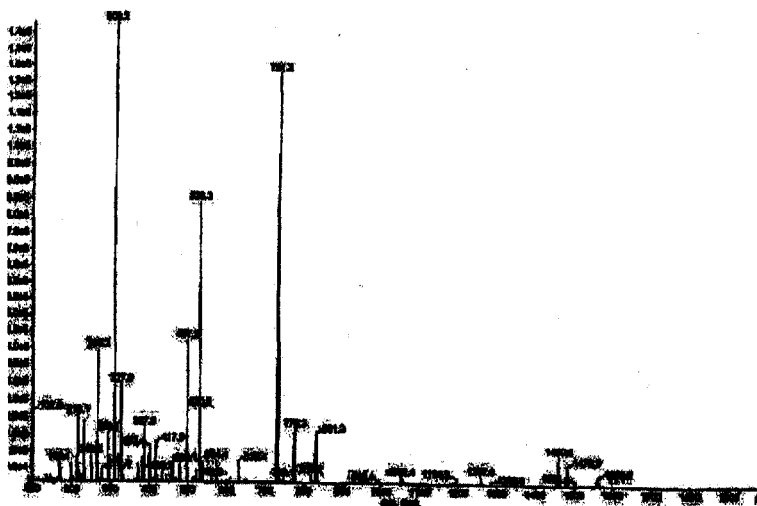


Figure IV - 2: Mass spectra of Hg-Triazine

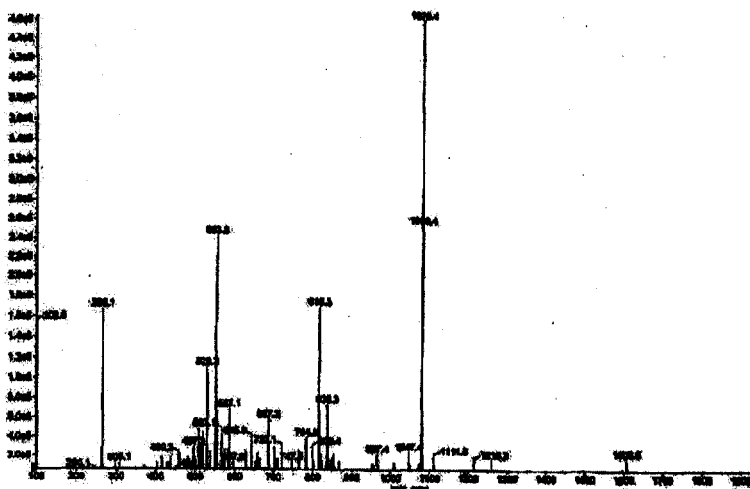


Figure IV - 3: Mass spectra of Sn-Triazine

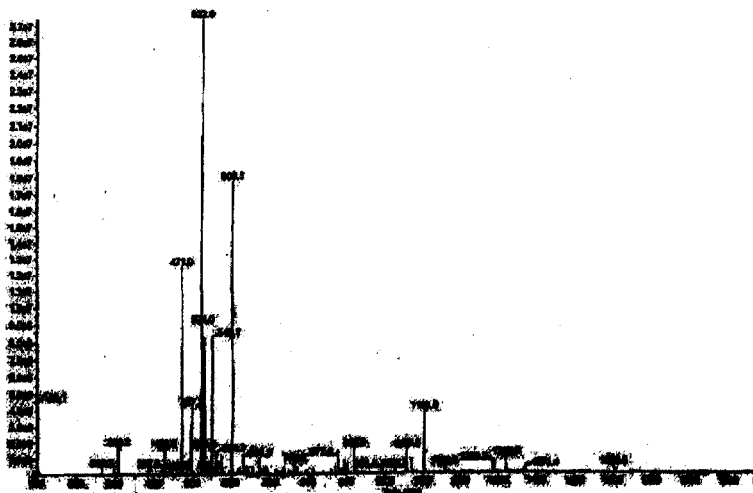


Figure IV - 4: Mass spectra of Th-Triazine

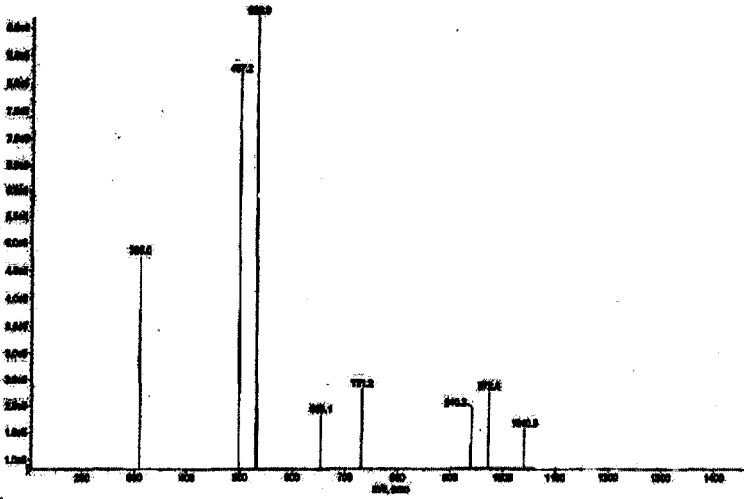
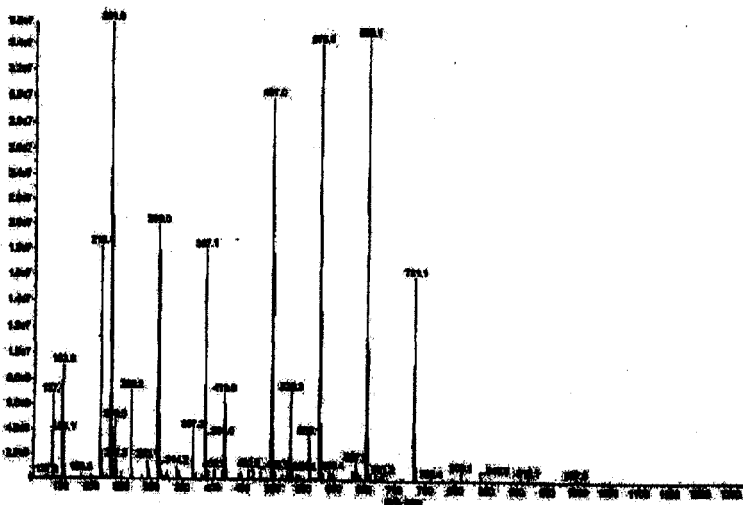
Figure IV - 5: Mass spectra of UO<sub>2</sub>-Triazine

Figure IV - 6: Mass spectra of W-Triazine

#### 4.2. Molar conductance

All the metal-triazine complexes prepared are insoluble in water and soluble in coordinating solvents. Molar conductances of complexes in present study are measured in DMF. It is reported that molar conductance values differ in different solvents and the expected range of molar conductance,  $\Lambda_M$  ( $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) for metal complexes in some common organic solvents at  $10^{-3}\text{M}$  are summarized by Geary [1]. In the present study the conductance values of all these complexes measured in DMF (concentration  $10^{-3}\text{M}$ ) fall in the range of 2.00- 11.50  $\text{Mho.cm}^2.\text{mol}^{-1}$ . The too low molar conductance values of complexes suggest that there is no dissociation of complexes in DMF. This indicates that the non electrolytic nature [1-3] of the triazine metal complexes. The values are presented in the Table IV-2.

#### 4.3. Magnetic Properties

Magnetic measurements pitch upon the electronic configuration of the d shell of the transition metal complexes. The magnetic susceptibility values (in BM) of metal complexes at room temperature are presented in Table IV-2.

(a) **Copper complex:** Irrespective of stereochemistry, Cu complexes possess one unpaired electron and the magnetic moment would be corresponding to this unpaired electron. But orbital angular momentum makes an additional contribution to a varying degree in different geometries and as a result the observed values are in the range 1.7 – 2.2 B.M. Figgis has predicted a magnetic moment value greater than 1.9 B.M. for tetrahedral and less than 1.9 B.M. for square planar and distorted octahedral geometries [4]. In the former case, orbital contribution is expected where as in the later no orbital contribution is possible by virtue of a non-degenerate ground state [5]. The magnetic moment values usually observed for square planar and tetrahedral complexes are little more than the spin only value of 1.73 B.M. which might be due to spin orbit coupling or due to the behavior of marked spin exchange of Cu (II) ions [6]. In the present investigation the observed magnetic moment value for Cu triazine complex is 1.81 B.M. which indicates that the complex may be in distorted octahedral geometry.

(b) **Tungsten complex:** The tungsten complex has a magnetic moment of 0.21 B.M. This low value of magnetic moment does not ascertain any unpaired electrons in the complex [7-9].

#### 4.4. Electronic spectra of complexes

The electronic spectra of complexes have been studied with a view to obtain more information on the configuration of these complexes. The typical electronic spectra of the studied complexes are reported in Figures IV-7 to IV-12. The absorption band maxima with their assignments are summarized in Table IV-2.

##### (a) Copper complex:

The copper triazine complex showed three bands in the region 18450.2, 19782.4 and 32258.1  $\text{cm}^{-1}$  which may be due to the transitions  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  (or  $d_{xy} \rightarrow d_{x^2-y^2}$  and  $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$  [10, 11]) respectively. These absorption bands in turn accord for distorted octahedral geometry in copper triazine complex as reported in previous studies [12, 13, 14-16]. The band at 18450.2  $\text{cm}^{-1}$  is a broad band and the broadening of the band may be attributed to Jahn-Teller distortion [17, 18]. Three spin allowed transitions are expected for Cu (II) in near IR and visible region (Lever, 1984) [19]. The bands are resolved by Gaussian analysis and assigned to  $2B_{1g} \rightarrow 2A_{1g}$ ,  $2B_{1g} \rightarrow 2B_{2g}$  and  $2B_{1g} \rightarrow 2E_g$  transitions in the order of increasing energy. The sequence of energy levels depends on the amount of distortion due to ligand field and Jahn-Teller effect [20].

##### (b) Tungsten complex:

Tungsten triazine compound exhibited one absorption band at 18870.17  $\text{cm}^{-1}$  that can be assigned as a d-d transition, in addition there are two intense bands at 29895.37 and 36101.08  $\text{cm}^{-1}$  which may be assigned as charge-transfer or intra ligand transitions [7-9].

The electronic absorption bands of other complexes are also presented in the Table IV-2, they also showed the regular spectral bands due to their electronic transitions between ground and excited states. The intense bands observed in mercury and tin triazine complexes may be attributed to the (MLCT) charge transfer by possible 4d or 5d electrons in to the empty  $\pi^*$  orbitals of ligand. The absorption bands observed in the visible region for uranium and thorium triazine complexes may be attributed to the charge transfer transitions.

Table IV-2: Conductance, Magnetic &amp; electronic spectral data of triazine complexes

S.No	Complex	Molar conductance	$\mu$ B.M.	UV Vis Bands		Assignments
				nm	cm-1	
1	Cu Triazine	11.3311	1.81	542.0	18450.2	2B1g $\rightarrow$ A1g
				505.5	19782.4	2B1g $\rightarrow$ 2B2g
				310.0	32258.1	2B1g $\rightarrow$ 2Eg
				261.5	38240.9	LMCT
				212.5	47058.8	LMCT
2	W Triazine	5.1505	0.21	510.0	19607.84	d $\rightarrow$ d
				334.5	29895.37	
				277.0	36101.08	
3	Hg Triazine	7.2107		525.5	19029.5	
				501.5	19940.18	
				460.0	21739.13	
				287.0	34843.21	
4	Sn Triazine	9.2709		687.5	14545.45	
				584.5	17108.64	
				435.5	22962.11	
				315.5	31695.72	
				261.0	38314.18	
5	UO <sub>2</sub> Triazine	4.1204		431.5	23174.97	
				310.5	32206.12	
				272.5	36697.25	
6	Th Triazine	2.0602		580.0	17241.38	
				429.5	23282.89	
				347.5	28776.98	
				268.5	37243.95	
				224.0	44642.86	



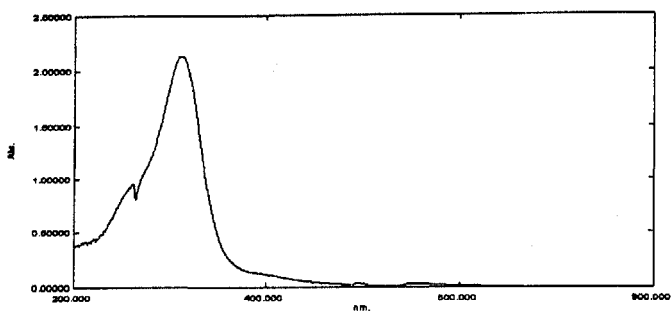


Figure IV - 7: Electronic spectra of Cu-Tiazine complex

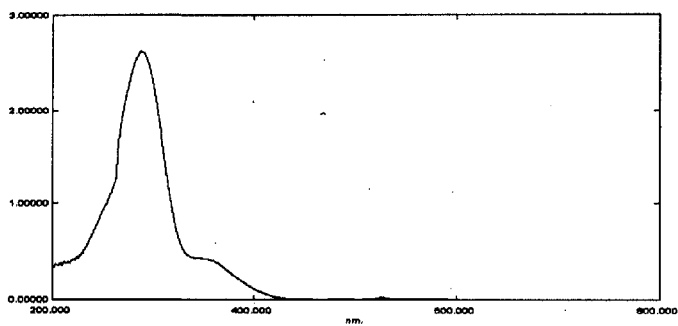


Figure IV - 8: Electronic spectra of Hg-Tiazine complex

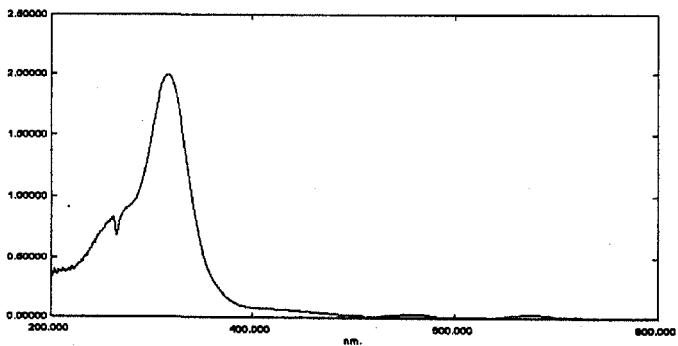


Figure IV - 9: Electronic spectra of Sn-Tiazine complex

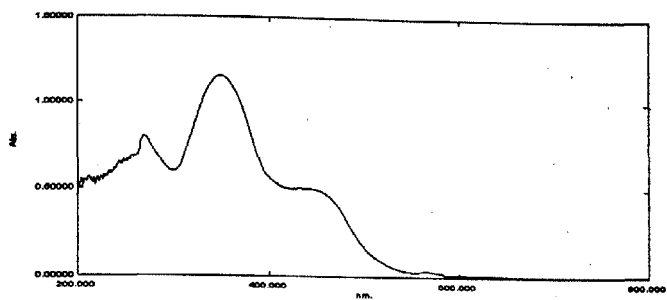


Figure IV - 10: Electronic spectra of Th-Tiazine complex

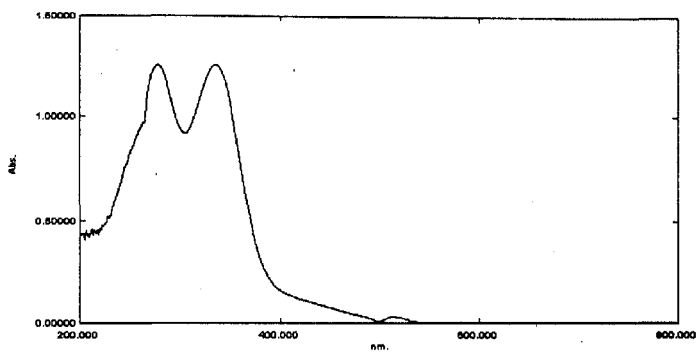


Figure IV - 11: Electronic spectra of W-Tiazine complex

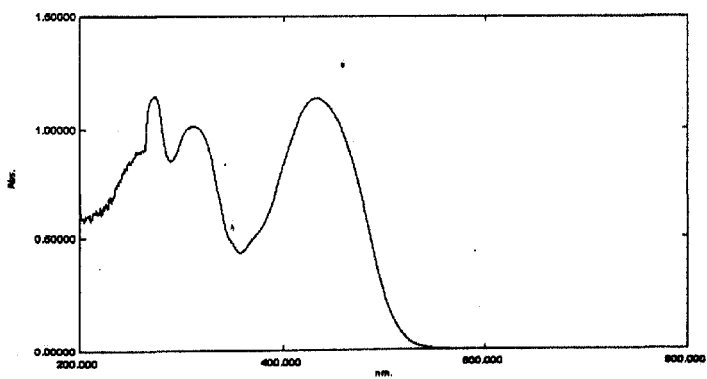


Figure IV - 12: Electronic spectra of UO<sub>2</sub>-Tiazine complex

#### 4.5. Infrared spectra

The IR spectra of all complexes were recorded and compared with that of ligand to study the structural changes in ligand upon complexation with metals and also to predict the coordination modes. The important IR frequencies of the ligand and its complexes are presented in Table IV-3. IR spectra of triazine metal complexes are shown in Figures IV-13 to IV-18.

IR spectra of all the metal complexes showed similar type of absorption bands which indicates that the coordination behaviour of ligand with all metals is same. This further shows that the coordinating sites present in the ligand (nitrogen and sulphur) are similarly reactive towards all the metals studied. The sharp strong band in the region  $3176\text{ cm}^{-1}$  which is a characteristic  $\nu$  (-NH) stretching frequency of the NH group of heterocyclic triazine ring was vanished in all complexes, suggesting coordination of nitrogen by deprotonation of NH. NH has high acidic character, to form bond with the metal ion in the view of previous assignments [21-23].

The IR spectrum of triazine is reported in Chapter-II, Figure II-2. The absence of a band in region  $2600\text{ cm}^{-1}$  in IR spectrum of ligand as well as any metal triazine complex suggest that the S (thioine) present in the ligand molecule is not in the form of thiol tautomer [22, 24]. The strong intensity band in the region  $1545\text{ cm}^{-1}$  and the corresponding weak intensity band at  $874.3\text{ cm}^{-1}$  may be assigned to thioamide (NC=S) [22-24] group present in the ligand. But in complexes the band corresponding to the above said CS moiety is shifted to lower frequencies ( $1495\text{s}$ - $1442\text{s}$  and  $869\text{w}$ - $769\text{w}$ ), indicating coordination of the sulfur in thioamide of triazine to the metal ion [22, 24, 25]. The other important band observed for all the metal triazine complexes at  $435 - 467\text{ cm}^{-1}$  may be attributed to  $\nu$  (M - N) as suggested by the previous reports [22, 25-27].

No appreciable change in  $\nu$  (C=N) and  $\nu_{\text{ring}}$  (C = C) frequencies [26, 28] upon complexation of ligand with metals indicates that the ring nitrogen (C=N) does not form metal nitrogen bonds with the metal ion. A group of medium intensity bands in the region  $1600 - 1500\text{ cm}^{-1}$  can be attributed to aromatic (C = C) of ligand as well as triazine metal complexes. The  $\nu$  (O - H) band appeared from  $3050$  to  $3450\text{ cm}^{-1}$  in the spectra of complexes indicates the existence of water molecules [26] which is also coincident with the results of the thermal analysis.

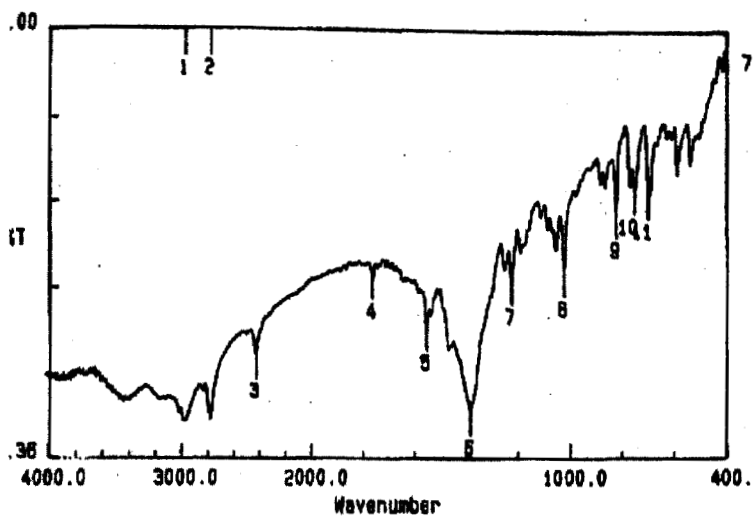


Figure IV - 13: IR spectra of Cu-Triazine complex

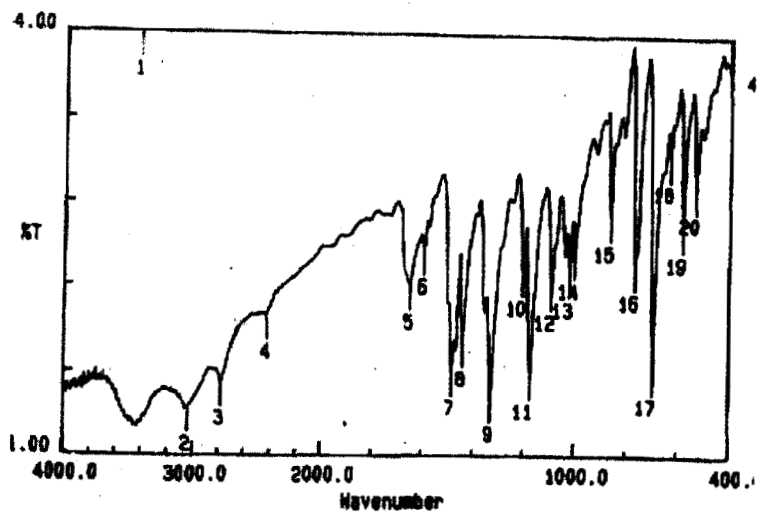


Figure IV - 14: IR spectra of Hg-Triazine complex

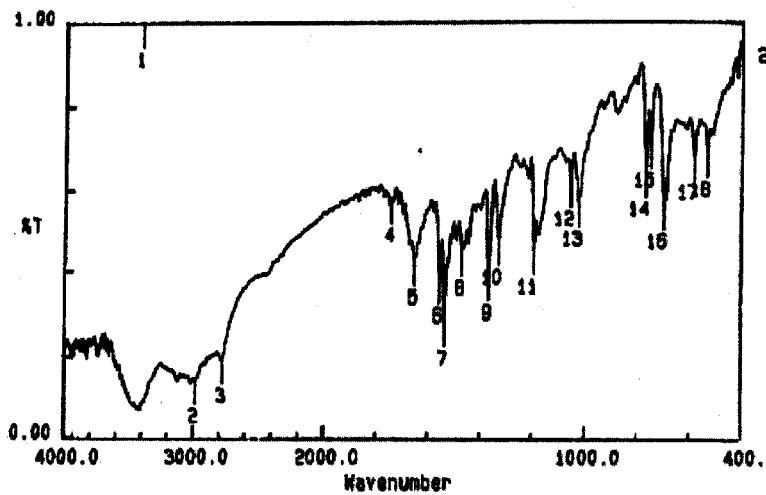


Figure IV - 15: IR spectra of Sn-Triazine complex

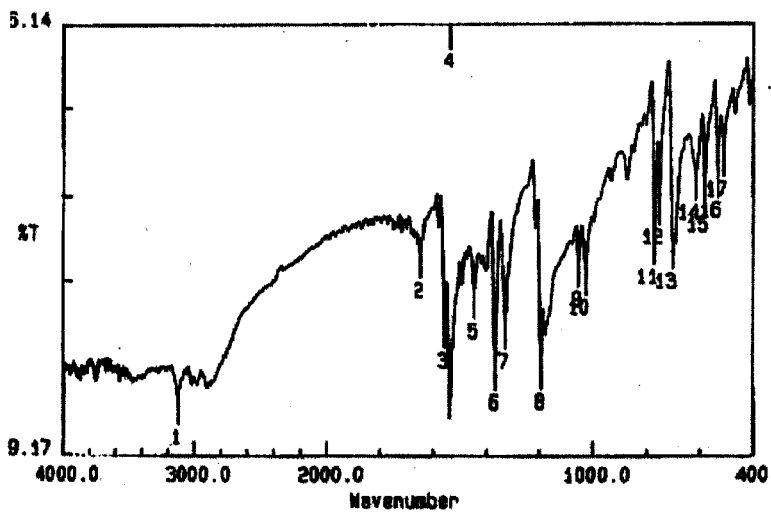


Figure IV - 16: IR spectra of Th-Triazine complex

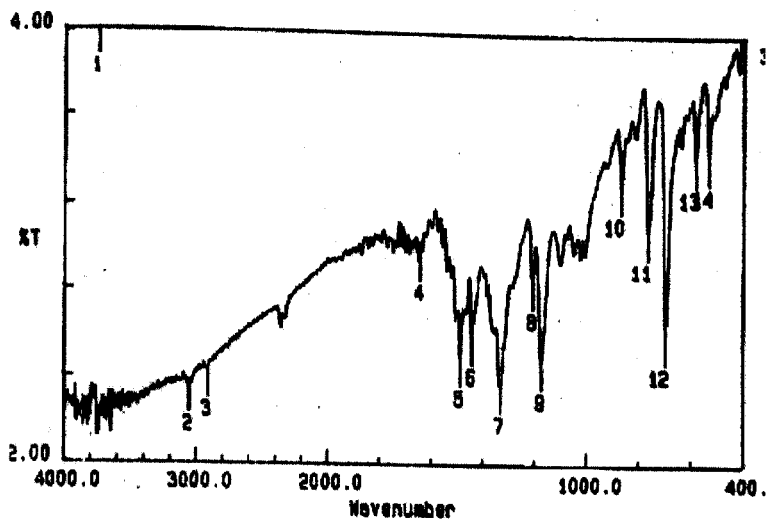
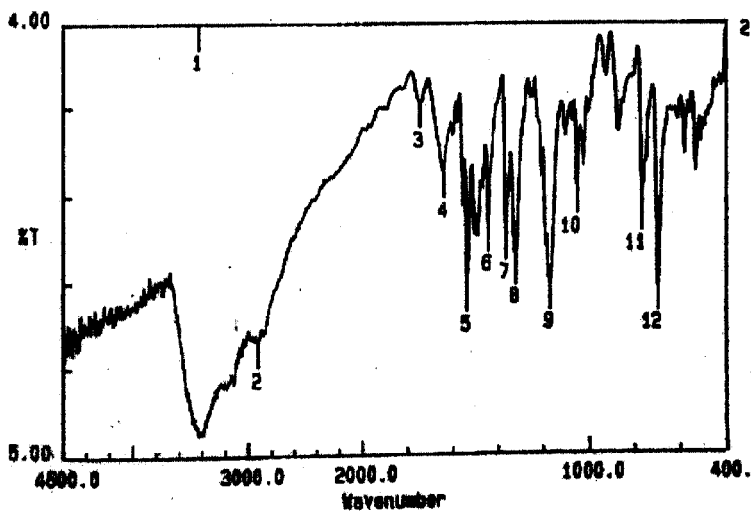
Figure IV - 17: IR spectra of UO<sub>2</sub>-Triazine complex

Figure IV - 18: IR spectra of W-Triazine complex

The remaining peaks are more or less not disturbed in the complexes in comparison with ligand. This shows the bidentate nature of the ligand in other words the metal attaches to the ligand through ring nitrogen and thione sulphur (one is C=S and other is protonated NH of C-NH-C) of ligand.

Table IV-3: IR Spectral data of triazine metal complexes

S.No	Compound	IR Values ( $\nu$ in $\text{cm}^{-1}$ )				
		NH	NC=S(thioamide)	C=N	C=C Ar	M-N
1	Triazine	3176	1545s, 874.3w	1659	1600 - 1500	-
2	Cu Triazine	-	1495s, 825.61w	1651	1600 - 1500	452
3	W Triazine	-	1442s, 769.67w	1651	1600 - 1500	435.24
4	Hg Triazine	-	1485s, 866.1w	1654	1600 - 1500	465.34
5	Sn Triazine	-	1471s, 769.6w	1647	1600 - 1500	448.71
6	U Triazine	-	1487s, 869.9w	1639	1600 - 1500	467.17
7	Th Triazine	-	1442s, 769.6w	1645	1600 - 1500	450.56

#### 4.6. $^1\text{H}$ NMR Spectra

The HNMR spectra of triazine ligand and its metal complexes are presented in Figures IV-19 to IV-24. The  $^1\text{H}$ NMR spectra of ligand and its triazine complexes were recorded in DMSO-d<sub>6</sub> solvent in the range of 0 - 12  $\delta$  (ppm) down field of TMS. The chemical shift values (ppm) with their assignments are given in Table IV-4.

The triazine did not show any resonance peak at ca. 4.0 – 4.4 ppm and also at 10 - 12 ppm, confirming the absence of –SH proton indicating absence of tautomerism of ligand to form SH group and confirming the presence of thione group (thioamide group) in the ligand [28]. The slight intense peak present at 9.3-9.4 in the ligand spectra is due to the –NH of the ring. The slight intensity may be due to fast exchange of protons between solvent and molecule as the compound is containing high acidic proton as reported by Kishore Kumar et al. [29]. In all the metal complexes of triazine the NH peak was absent which may be attributed to the deprotonation of the highly acidic proton to form bond with metals through nitrogen coordination [22].

The other aromatic region peaks are shifted slightly lower field due to coordination [30] of ligand with metal, which increased electron density. This factor reinforced the complexation process between ligand (triazine) and metals.

Table IV-4: HNMR Spectral data of triazine complexes.

S.No	Compound	H NMR Assignments (ppm)			
		SH	NH	Ar ring H	Other peaks
1	Triazine	-	9.3 - 9.4	7.17 - 7.52	3.5, 3.7, 2.4, 1.4, 1.6
2	Cu Triazine	-	-	7.21 - 7.63	Slight distortions
3	W Triazine	-	-	7.24 - 7.49	Slight distortions
4	Hg Triazine	-	-	7.19 - 7.54	Slight distortions
5	Sn Triazine	-	-	7.21 - 7.58	Slight distortions
6	U Triazine	-	-	7.19 - 7.56	Slight distortions
7	Th Triazine	-	-	7.19 - 7.58	Slight distortions



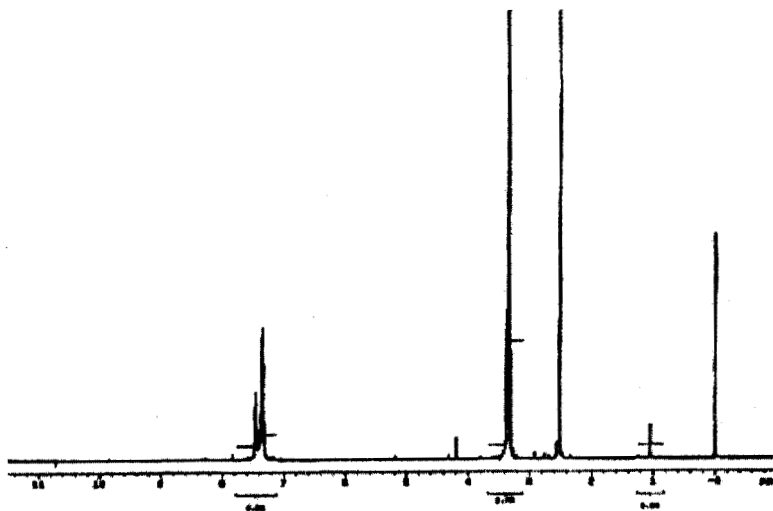


Figure IV - 19: HNMR spectra of Cu-Triazine complex

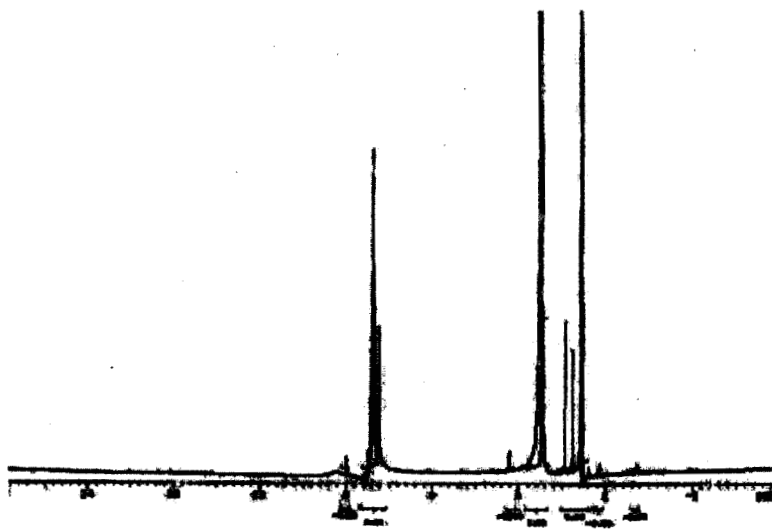


Figure IV - 20: HNMR spectra of Hg-Triazine complex

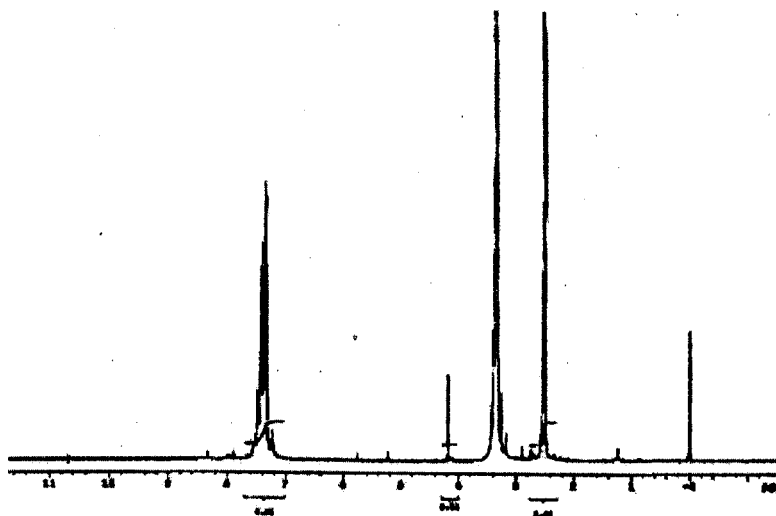


Figure IV - 21: HNMR spectra of Sn-Triazine complex

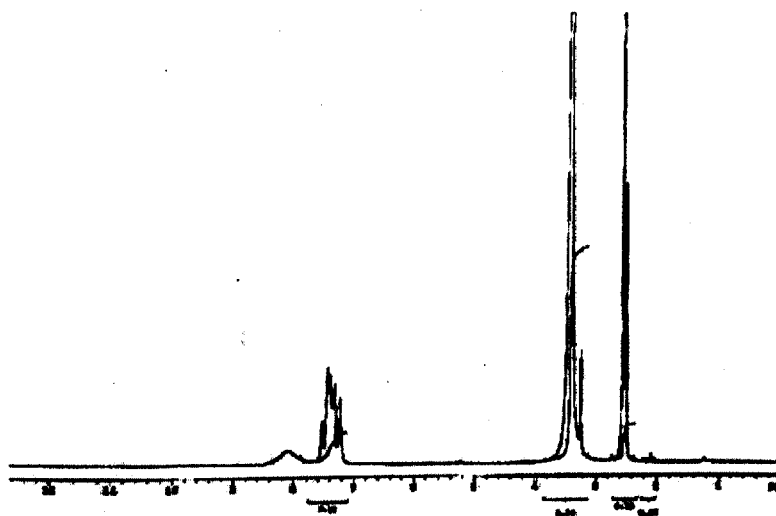


Figure IV - 22: HNMR spectra of Th-Triazine complex

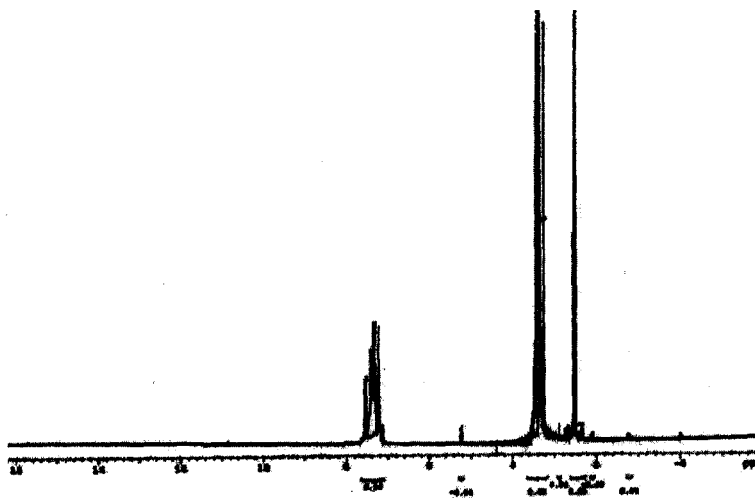
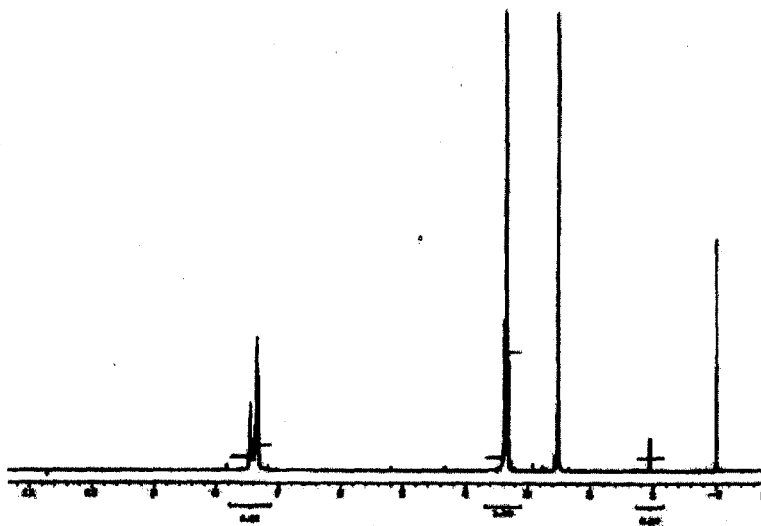
Figure IV - 23: HNMR spectra of  $\text{UO}_2$ -Triazine complex

Figure IV - 24: HNMR spectra of W-Triazine complex

#### 4.7. XPS studies:

X-Ray photoelectron spectroscopic study of Copper triazine complex was carried out and the corresponding XPS spectrum is presented in Figure IV-25.

In XPS studies the binding energy peak at 932.5 eV corresponds to Cu 2P of  $\text{Cu}^+$  [31]. Similarly the core level  $2p_{1/2}$  and  $2p_{3/2}$  energy levels at 952.4 and 932.6 eV. are reported for Cu (II) [32]. In the XPS studies of Cu complexes Wang et al. [33] reported Cu (II) peaks at binding energies of 394.9 – 395.4 combine with another peak at 954.4 – 955.1 eV. Xue et. al. [34] reported that the Cu(II) shows binding energy peak at 935.1 eV. and Cu (I) shows an intense peak with split at 932.9 eV. In the present study, Cu triazine complex showed two peaks at 934.2 and 953.9 eV. These peaks confirm that the Cu in copper triazine complex is in (II) oxidation state.

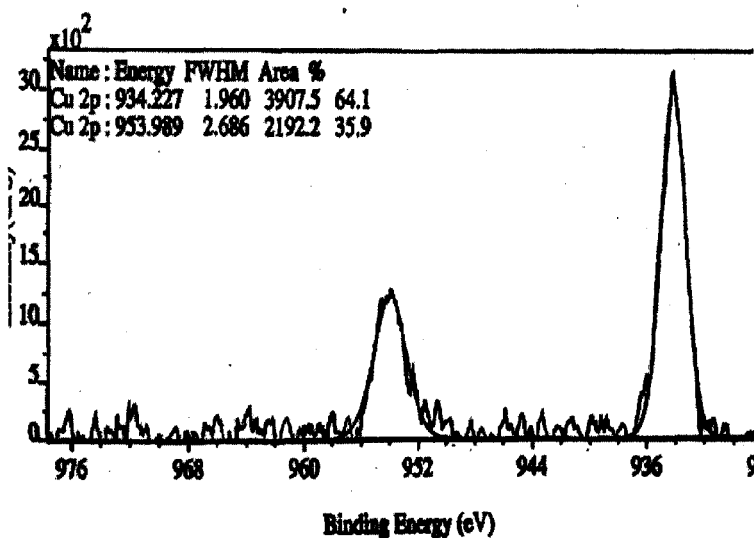


Figure IV-25: XPS spectra of Cu-Triazine complex

#### 4.8. TG - DTA Spectra

In the present investigation TG/DTA analysis was carried out under nitrogen atmosphere with a heating rate of at  $10\text{ }^{\circ}\text{C} / \text{min}$  and the weight loss was measured from the ambient temperature to  $800\text{ }^{\circ}\text{C}$ . The thermograms of all the triazine metal complexes are presented in figures IV-26 to IV-31. TG/DTA spectra of all triazine metal complexes shows that the initial weight loss was occurred in the region of  $100\text{--}280\text{ }^{\circ}\text{C}$ . due to the loss of moisture as hydrated water molecule. In tin, tungsten, mercury and thorium triazine complexes the lost water molecules has coordinating nature i.e. the water molecules were present inside the coordination sphere. It is also consistent with the DTA peaks present in the spectrum. The thermogram above the temperature  $400\text{ }^{\circ}\text{C}$  is almost horizontal (except for tin, thorium and uranium triazine complexes where horizontal TG graph starts almost above  $900\text{ }^{\circ}\text{C}$ .) indicating the decomposition temperature of complexes.

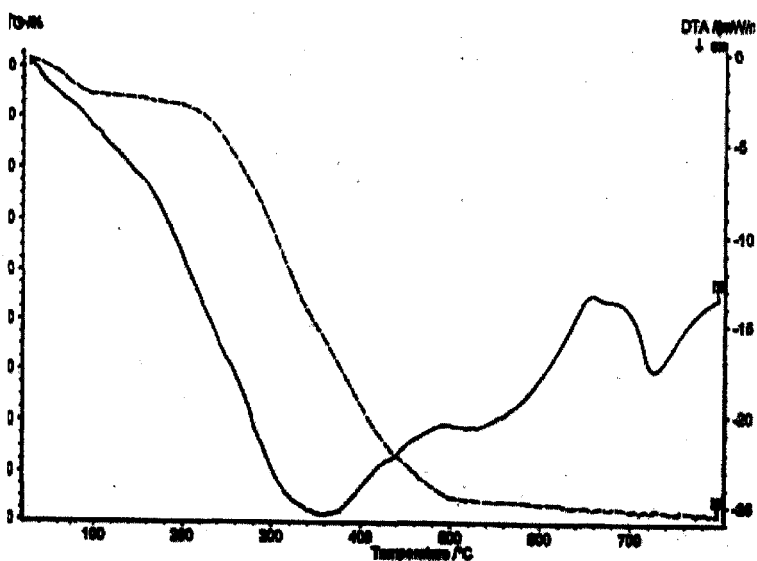


Figure IV - 26: TG / DTA spectrum of Hg -Triazine complex

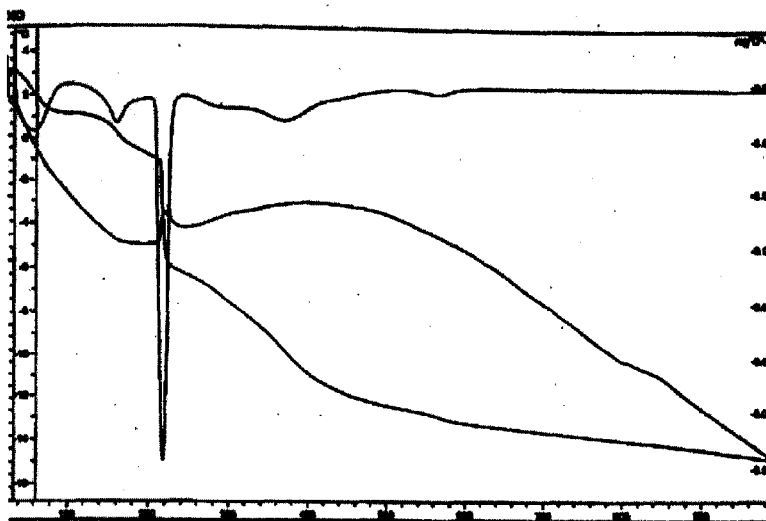


Figure IV - 27: TG/DTA spectrum of Th-Triazine complex

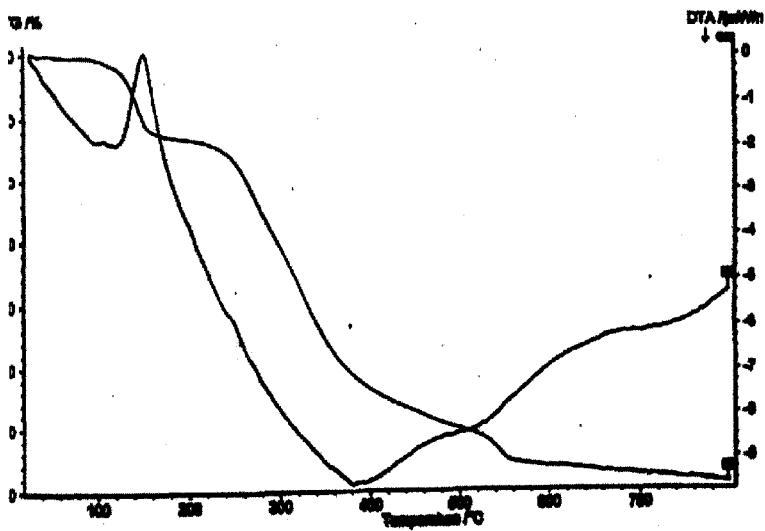


Figure IV - 28: TG/DTA spectrum of W-Triazine complex

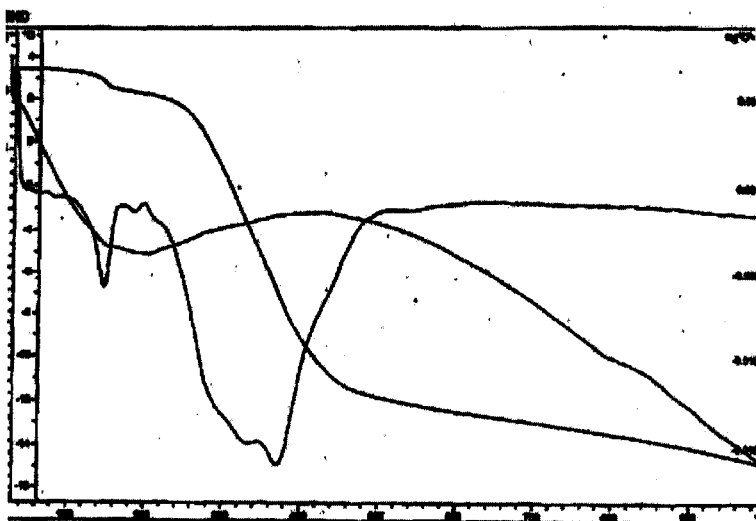
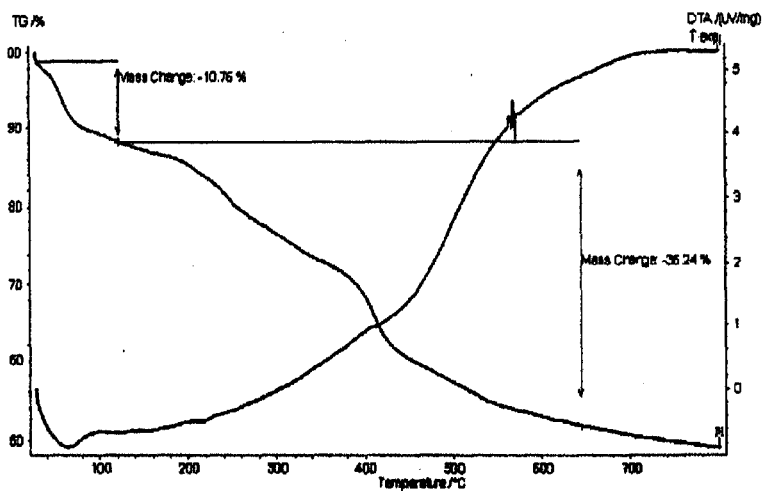
Figure IV - 29: TG/DTA spectrum of  $\text{UO}_2$ -Triazine complex

Figure IV - 30: TG/DTA spectrum of Cu-Triazine complex

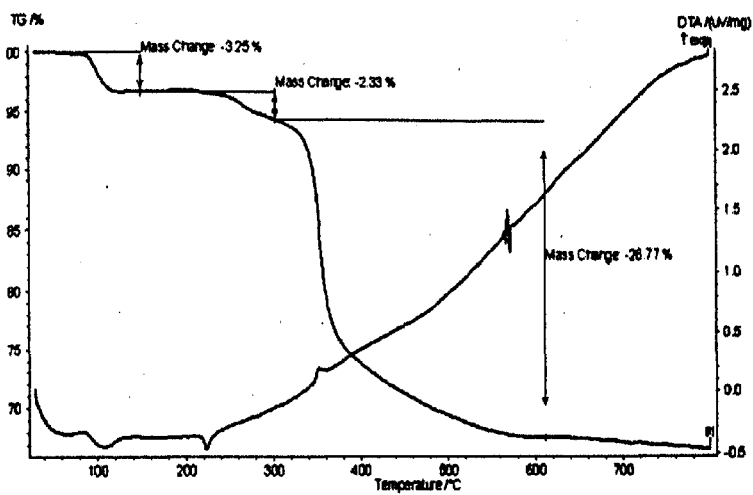


Figure IV - 31: TG/DTA spectrum of Sn-Triazine complex



#### 4.9. Stability constants determination

In the present investigation evidence for the formation of complexes of triazine with copper, tungsten, mercury, tin uranium and thorium metals in solutions has been obtained from the pH titration curves. The pH data of titrations of triazine and its metal solutions versus base (0.1 M KOH) and corresponding pH metric curves are presented in Table IV-5 and Figure IV-32 respectively. The values of  $n$ , pH and pL for obtaining  $\log K_1$  and  $\log K_2$  values of metal complexes are presented in Table IV-6(a) and (b). The following features of the pH data confirm the formation of complexes for all the metal ions studied.

1. A decrease in pH was observed when a solution of metal ions is added to the ligand solution, suggesting the liberation of protons as a result of complexation.
2. In the pH titration of ligand and ligand metal ions, it is found that the metal-ligand titration curve runs always below the ligand titration curve indicating the complex formation.
3. In all the metal ions studied, the pH of the hydrolysis of the metal ions is noted by titrating acidified metal ions. The metal ligand curve diverges from the ligand curve before the hydrolysis of metal ions. In the presence of ligand, the hydrolysis of metal ions is found to occur at a higher pH than in the absence of ligand.
4. During titration the equilibrium is attained rapidly.
5. There is a shift in pH of precipitation during the formation of binary complex and also intensification of colour was observed as a result of complex formation.

The above mentioned salient feature of the pH titration data is a clear indication of the formation of complexes in solution by all metal ions.

Table IV-5: pH titration data of acid, ligand and metals binary system in 75 % dioxan medium at 303 K and 0.1 M ionic strength.

[HNO<sub>3</sub>] = 4.0x10<sup>-3</sup> M  
 [triazine] = 1x10<sup>-3</sup> M  
 [metal] = 2x10<sup>-3</sup> M  
 [KOH] = 1x10<sup>-1</sup> M

Ionic strength = 0.1 M  
 Total volume = 50 ml  
 Temperature = 303 K

volume of base KOH	PH							
	Acid	Triazine	Cu	W	Hg	Sn	Th	U
0.00	2.96	2.68	2.34	2.73	2.62	2.59	2.72	2.71
0.10	3.03	2.74	2.38	2.79	2.66	2.64	2.80	2.80
0.20	3.08	2.77	2.42	2.79	2.72	2.68	2.85	2.86
0.30	3.11	2.79	2.46	2.81	2.77	2.70	2.93	2.89
0.40	3.08	2.84	2.47	2.84	2.82	2.75	2.96	2.92
0.50	3.14	2.89	2.49	2.87	2.82	2.78	3.03	3.00
0.60	3.17	2.90	2.52	2.90	2.86	2.80	3.05	3.02
0.70	3.20	2.97	2.55	2.96	2.89	2.84	3.13	3.07
0.80	3.25	3.02	2.58	3.03	2.93	2.91	3.20	3.13
0.90	3.32	3.11	2.61	3.09	3.02	2.94	3.31	3.19
1.00	3.35	3.10	2.59	3.14	3.03	2.98	3.42	3.26
1.10	3.41	3.22	2.63	3.19	3.07	3.02	3.52	3.36
1.20	3.50	3.35	2.63	3.24	3.14	3.08	3.69	3.46
1.30	3.56	3.38	2.69	3.28	3.21	3.14	3.81	3.64
1.40	3.72	3.58	2.69	3.32	3.32	3.25	3.99	3.79
1.50	3.93	3.68	2.71	3.41	3.39	3.39	4.01	4.05
1.60	4.58	4.12	2.73	3.46	3.52	3.48	4.35	4.34
1.70	5.67	4.51	2.76	3.52	3.72	3.61	4.85	4.62
1.80	6.45	6.23	2.80	3.58	4.14	3.87	5.50	4.77
1.90	7.63	7.22	2.82	3.75	5.17	4.65	6.27	5.02
2.00	9.60	8.52	2.88	4.57	6.98	6.25	7.22	5.11
2.10	11.08	9.62	2.93	6.28	7.17	6.80	8.29	5.20
2.20	11.47	10.13	2.94	7.52	7.84	7.65	9.10	5.31
2.30	11.80	10.53	2.95	8.76	8.36	8.90	9.62	5.41
2.40	12.13	10.76	2.98	9.91	8.97	9.62	9.93	5.51
2.50	12.21	11.10	2.99	10.45	10.06	10.05	10.13	5.56
2.60	12.31	11.42	3.04	10.52	10.24	10.55	10.48	5.63
2.70	12.49	11.71	3.11	11.18	10.35	10.80	10.53	5.69
2.80	12.61	11.79	3.14	11.72	11.07	11.16	10.70	5.73
2.90	12.65	11.97	3.19	11.84	11.20	11.43	10.88	5.81
3.00	12.72	12.06	3.25	11.93	11.46	11.68	10.93	5.84
3.10	12.76	12.12	3.29	12.04	12.16	11.84	11.23	5.89
3.20		12.24	3.39	12.16	12.22	11.94	11.33	5.95
3.30		12.28	3.45	12.24	12.25	11.99	11.60	6.00
3.40		12.29	3.60	12.28	12.32	12.16	11.72	6.03
3.50		12.33	3.67	12.32	12.34	12.16	11.89	6.08
3.60		12.39	3.82		12.35	12.19	11.95	6.13
3.70		12.41	4.06		12.38	12.32	12.06	6.20
3.80		12.43	4.81			12.38	12.13	6.24
3.90		12.47	6.70			12.42	12.23	6.29
4.00		12.48	8.75	12.49	12.48	12.44		6.35
4.10		12.52	10.00			12.49	12.24	6.41
4.20		12.55	10.30			12.50		6.46

4.30		12.56	10.87			12.51		6.52
4.40			11.15			12.54		6.57
4.50		12.59	11.50	12.61	12.60	12.60	12.48	6.62
4.60			11.51					6.73
4.70			11.75					6.80
4.80			11.80					6.95
4.90			11.92					7.03
5.00		12.68	12.01	12.70	12.66	12.71	12.60	7.15
5.10			12.08					7.60
5.20								8.20
5.30								9.58
5.40								9.96
5.50			12.60					10.11
5.60								10.95
5.70								11.12
5.80								11.27
5.90								11.26
6.00			12.43					11.57
6.10								11.70
6.20								11.80
6.30								11.89
6.40								11.96
6.50			12.54					12.00
6.60								12.06
6.70								12.10
6.80								12.12
6.90								12.16
7.00								12.20
7.10								12.28
7.20								12.35

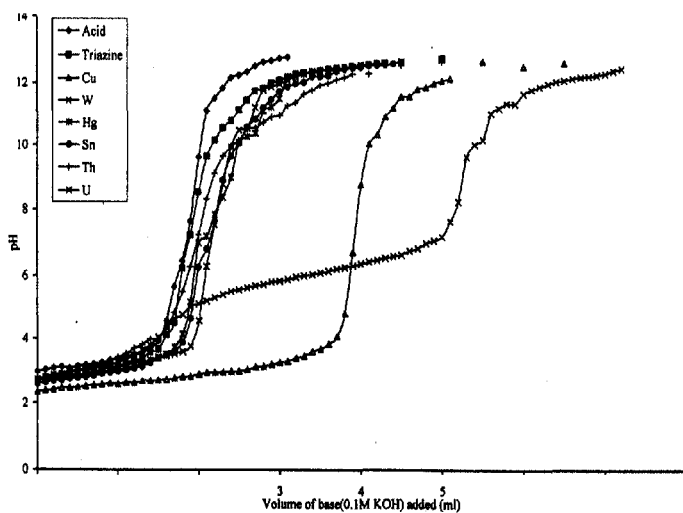


Figure III-32: pH titration curves of acid, ligand and metals

Table III-6(a): Data for obtaining stability constants of Triazine complexes

Sn			Th			U		
pH	n	pL	pH	n	pL	pH	n	pL
3.50	3.70	10.65	3.50	3.14	10.82	3.50	2.15	10.30
3.60	3.06	10.38	3.60	2.73	10.30	3.60	1.34	10.10
3.70	2.61	10.18	3.70	3.14	10.29	3.70	1.73	10.05
3.80	2.64	10.09	3.80	2.44	10.05	3.80	1.21	9.88
3.90	2.51	9.97	3.90	2.08	9.89	3.90	1.05	9.76
4.00	2.36	9.84	4.00	1.07	9.67	4.00	0.80	9.64
4.10	2.14	9.71	4.10	0.71	9.53	4.10	0.75	9.53
4.20	2.07	9.60	4.20	0.48	9.41	4.20	0.53	9.41
4.30	1.90	9.47	4.30	0.53	9.31	4.30	0.51	9.31
4.40	1.88	9.37	4.40	0.51	9.21	4.40	0.38	9.20
4.50	1.75	9.25	4.50	0.72	9.13	4.50	0.42	9.10
4.60	1.86	9.17	4.60	0.47	9.01	4.60	0.07	8.97
4.70	1.84	9.07	4.70	0.39	8.90	4.70	0.46	8.91
4.80	1.80	8.96	4.80	0.25	8.79	4.80	0.89	8.85
4.90	1.80	8.86	4.90	0.08	8.67	4.90	1.21	8.79
5.00	1.78	8.76	5.00	0.02	8.57	5.00	1.49	8.72
5.10	1.75	8.65	5.10	0.08	8.47	5.10	0.94	8.74
5.20	1.78	8.56	5.20	0.19	8.38	5.20	1.02	8.83
5.30	1.82	8.46	5.30	0.27	8.29	5.30	1.17	8.97
5.40	1.70	8.35	5.40	0.22	8.18	5.40	1.23	9.58
5.50	1.84	8.27	5.50	0.44	8.11	5.50	1.29	8.81
5.60	1.78	8.16	5.60	0.48	8.01	5.60	1.34	8.33
5.70	1.76	8.05	5.70	0.53	7.91	5.70	1.04	7.98
5.80	1.73	7.95	5.80	0.56	7.82	5.80	1.01	7.77
5.90	1.79	7.86	5.90	0.69	7.73	5.90	1.21	7.52
6.00	1.82	7.76	6.00	0.77	7.64	6.00	1.38	7.33
6.10	1.82	7.66	6.10	0.83	7.54	6.10	1.58	7.14
6.20	1.77	7.56	6.20	0.77	7.44	6.20	1.78	6.97
6.30	1.92	7.48	6.30	0.89	7.35	6.30	1.97	6.81
6.40	2.04	7.40	6.40	0.95	7.26	6.40	2.12	6.67
6.50	2.09	7.30	6.50	0.90	7.15	6.50	2.35	6.52
6.60	2.22	7.22	6.60	0.97	7.06	6.60	2.55	6.37
6.70	2.22	7.12	6.70	0.89	6.95	6.70	2.63	6.26
6.80	2.42	7.06	6.80	1.01	6.86	6.80	2.85	6.12
6.90	2.41	6.95	6.90	0.92	6.76	6.90	2.90	6.01
7.00	2.54	6.88	7.00	1.05	6.67	7.00	3.00	5.89
7.10	2.56	6.78	7.10	1.03	6.57	7.10	3.14	5.77
7.20	2.58	6.68	7.20	1.00	6.46	7.20	3.24	5.65
7.30	2.69	6.60	7.30	1.04	6.37	7.30	3.26	5.55
7.40	2.67	6.50	7.40	1.07	6.27	7.40	3.30	5.44
7.50	2.75	6.42	7.50	1.10	6.18	7.50	3.35	5.34
7.60	2.88	6.34	7.60	1.13	6.08	7.60	3.44	5.22
7.70	2.88	6.24	7.70	1.17	5.98	7.70	3.41	5.13
7.80	2.99	6.16	7.80	1.24	5.89	7.80	3.46	5.02
7.90	2.96	6.06	7.90	1.29	5.80	7.90	3.47	4.92
8.00	2.93	5.95	8.00	1.28	5.70	8.00	3.48	4.82

Table III-6(b): Data for obtaining stability constants of triazine complexes

Cu			W			Hg		
pH	n	pL	pH	N	pL	pH	N	pL
3.50	2.88	9.40	3.50	2.21	10.31	3.50	3.27	10.52
3.60	2.09	9.48	3.60	1.51	10.12	3.60	2.44	10.25
3.70	2.23	9.34	3.70	1.97	10.08	3.70	2.14	10.11
3.80	2.20	9.25	3.80	1.71	9.94	3.80	2.02	9.99
3.90	2.11	9.17	3.90	1.46	9.81	3.90	1.92	9.87
4.00	1.99	9.11	4.00	1.46	9.71	4.00	1.89	9.77
4.10	1.96	9.01	4.10	1.65	9.64	4.10	1.77	9.66
4.20	1.90	8.94	4.20	1.60	9.53	4.20	1.72	9.55
4.30	1.89	8.84	4.30	1.79	9.46	4.30	1.55	9.43
4.40	1.88	8.74	4.40	1.85	9.36	4.40	1.46	9.32
4.50	1.97	8.61	4.50	2.22	9.32	4.50	1.27	9.19
4.60	1.94	8.52	4.60	1.99	9.18	4.60	1.34	9.10
4.70	1.92	8.43	4.70	1.99	9.08	4.70	1.36	9.00
4.80	1.87	8.34	4.80	1.95	8.98	4.80	1.33	8.90
4.90	1.86	8.25	4.90	1.83	8.86	4.90	1.45	8.82
5.00	1.82	8.16	5.00	1.83	8.76	5.00	1.43	8.71
5.10	1.83	8.06	5.10	1.82	8.66	5.10	1.46	8.62
5.20	1.83	7.96	5.20	1.79	8.56	5.20	1.49	8.52
5.30	1.85	7.85	5.30	1.83	8.46	5.30	1.47	8.42
5.40	1.87	7.74	5.40	1.90	8.37	5.40	1.37	8.31
5.50	1.89	7.64	5.50	1.79	8.26	5.50	1.49	8.22
5.60	1.87	7.54	5.60	1.82	8.16	5.60	1.52	8.12
5.70	1.87	7.44	5.70	1.84	8.06	5.70	1.40	8.01
5.80	1.87	7.34	5.80	1.78	7.95	5.80	1.44	7.91
5.90	1.88	7.24	5.90	1.78	7.85	5.90	1.44	7.81
6.00	1.87	7.14	6.00	1.75	7.75	6.00	1.47	7.72
6.10	1.87	7.04	6.10	1.69	7.64	6.10	1.47	7.62
6.20	1.92	6.93	6.20	1.86	7.57	6.20	1.40	7.51
6.30	1.94	6.82	6.30	1.74	7.45	6.30	1.46	7.42
6.40	1.93	6.73	6.40	1.70	7.34	6.40	1.43	7.31
6.50	1.99	6.61	6.50	1.85	7.26	6.50	1.39	7.21
6.60	1.99	6.51	6.60	1.82	7.16	6.60	1.39	7.11
6.70	1.97	6.41	6.70	1.88	7.07	6.70	1.27	6.99
6.80	2.05	6.29	6.80	1.87	6.97	6.80	1.34	6.90
6.90	2.04	6.19	6.90	1.94	6.88	6.90	1.22	6.79
7.00	2.04	6.09	7.00	1.84	6.76	7.00	1.22	6.69
7.10	2.08	5.98	7.10	1.90	6.67	7.10	1.18	6.58
7.20	2.10	5.88	7.20	2.01	6.59	7.20	1.15	6.48
7.30	2.10	5.78	7.30	1.90	6.47	7.30	1.12	6.38
7.40	2.12	5.67	7.40	1.88	6.37	7.40	1.02	6.27
7.50	2.15	5.57	7.50	1.87	6.27	7.50	1.07	6.17
7.60	2.18	5.46	7.60	1.90	6.17	7.60	0.96	6.06
7.70	2.16	5.36	7.70	1.80	6.06	7.70	0.98	5.96
7.80	2.18	5.26	7.80	1.79	5.96	7.80	1.00	5.86
7.90	2.19	5.15	7.90	1.72	5.85	7.90	1.00	5.76
8.00	2.18	5.06	8.00	1.68	5.74	8.00	0.90	5.65

The stability constants of the triazine metal complexes were determined by the pH metric method and corresponding free energies of triazine metal complexes were calculated and the respective data are presented in the Table IV-7. The calculation of the stability constants ( $\log K_1$  and  $\log K_2$ ) of the investigated metal complexes is based on the fact that the pH measurements during the titration of a ligand solution in presence and in absence of a metal ion could be used to calculate the free base exponent (pL) and the number of ligand molecules attached per metal ion ( $\bar{n}$ ). The Irving-Rossetti relations [35]:

$$\log(\bar{n}/1-\bar{n}) = \log K_1 - pL \quad \text{and} \quad \log(\bar{n}-1/2-\bar{n}) = \log K_2 - pL$$

have been constructed and analyzed to determine  $\log K_1$  and  $\log K_2$ , respectively. The interaction of the studied ligand transition metal ions (copper and tungsten), heavy metal ions (mercury and tin) and 5f actinide metal ions (uranium and thorium) have been studied potentiometrically in 75% (v/v) dioxan-water at 303K using 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> as a supporting electrolyte. The stability constants and Gibbs free energy values are summarized in Table IV-8. Analysis of the data reveals [36, 37] the following aspects.

- (i)  $K_1/K_2 > 1.0$  for tungsten triazine complex indicating that the coordination sites on the ligands for complexation of metal ion with one triazine molecule and further binding of metal with second triazine molecule is somewhat difficult due to steric hindrance for the second coordination.
- (ii)  $K_1/K_2 < 1.0$  for complexes of copper, mercury, tin, uranium and thorium triazine suggesting their free coordination with two triazine molecules without steric hindrance, which is consistent with their higher coordination numbers.

Table IV-7: Stability constants of triazine complexes

S.No	Complex	$\log K_1$	$\log K_2$	$\log \beta$	$K_1/K_2$	$-\Delta G$ (KJ/mol)
1	Triazine	10.55	-	-	-	-
2	Cu Triazine	0.50	0.60	1.10	0.83	6.38
3	W Triazine	10.99	5.48	16.47	2.01	95.55
4	Hg Triazine	4.81	7.50	12.31	0.64	71.42
5	Sn Triazine	2.20	3.00	5.20	0.73	30.17
6	U Triazine	6.26	6.35	12.61	0.99	73.16
7	Th Triazine	7.32	7.51	14.83	0.98	81.17

#### 4.10. Analytical application of the reagent

The triazine (5,6-Diphenyl-2H-[1,2,4]triazine-3-thione) synthesized was studied for its analytical application by using the reagent for the determination of copper in different matrices.

Copper reacts with triazine and form copper-triazine complex at pH 5.5 which is freely soluble in dil. HCl. This formed the basis for the development of solid phase extraction method for the preconcentration of copper from environmental samples and determined by AAS.

##### 4.10.1. Effect of pH

The effect of pH on the preconcentration of Cu on Amberlite XAD-16 resin functionalized with triazine was studied. The pH of the solution was adjusted by using 1 mol/L HCl between pH 1.0 and 4.0, 0.2 mol/L acetate buffer between pH 4.0 and 6.0, borate buffer at pH 7.0, and ammonium buffer between pH 8.0 and 10.0. The preconcentration and analysis of Cu was carried out as described in the general procedure described in Chapter II, Section 2.11. The data was shown in Figure IV-33. The recoveries were higher when pH was between 5.0-6.0. Hence a pH of 5.5 was chosen for the preconcentration of Cu metal ions in water samples.

##### 4.10.2. Effect of HCl concentration on elution

The effect of HCl concentration on elution of Cu ions from resin was studied by carrying out the elution of copper from the resin with 0.2 – 4.0 M HCl. The results indicated that elution is dependent on the concentration of HCl. Highest recovery (99.6 %) was obtained with 2, 2.5 mol/L HCl solution as shown in Figure IV-34. Therefore, 10 ml of 2 M HCl was selected for elution of Cu from the column.

##### 4.10.3. Effect of Flow rate and eluent

The metal ion sorption on Amberlite XAD-16 functionalized with triazine was studied at different flow rates of the solution. A set of solutions (50 mL) containing 5 µg of Cu metal ion were taken and the solution pH was adjusted to 5.5, then solutions were passed through a resin-loaded column at a flow rate of 1 to 4 ml/min. The metal ions from the resin were desorbed with 2 M HCl (10 mL). The metal content of eluate was determined as mentioned in the recommended procedure. It was found that the

optimum flow rate for Cu ions was 2 mL/min from Figure IV-35(a). However at a flow rate greater than 2 mL, there was a decrease in percentage sorption.

Similarly the rate of eluent was determined by desorbing the sorbed Cu ions from column with 2 M HCl solution at a flow rate of 1 to 4ml/min. It was found that the optimum flow rate of eluent for Cu ions desorption was 1 ml/min as revealed from Figure IV-35(b). However at a flow rate greater than 2 ml, there was a decrease in percentage of desorption.

#### 4.10.4. *Efficiency of sorption, spike recovery and preconcentration factor*

The efficiency of sorption is expressed as the concentration of the analyte retained on the sorbent during preconcentration. The quantitative sorption of Cu(II) from standard solution was studied by taking 20 µg of metal in a 100 ml sample and passing it through the 1 g of AXAD-16 functionalized triazine resin. The Cu metal sorbed on triazine-coated resin was eluted with 2 M HCl and determined by AAS method. The results are presented in Table IV-8. The detection limit, expressed as the amount of analyte in µg/L giving a signal-to-noise ratio of 3. The detection limit was 0.8 µg/l. The recovery was found to be 99.12 % as shown in Table IV-9 (mean and standard deviation after four replicate measurements).

The preconcentration factor was determined by increasing the dilution of metal solution while keeping the total amount of metal ion fixed at 50 µg i.e. calculated from the ratio of highest sample volume and quantitative recovery to 10 ml final volume. The preconcentration factor for this study was found to be 180.

#### 4.10.5. *Resin regenerative and durability nature*

Accuracy and reproducibility in analytical data is a challenging task on reusing the same resin. In order to study these effects, 500 mg of resin was equilibrated with (100 ml; 50 µg/ml) metal ion solution under optimum experimental conditions. After desorption and determination process, the results were tested for reproducibility and it was found to be within 3.5 % RSD over 10 cycles (as depicted in Figure IV-36) thereby reflecting the reliability and reproducibility of the resin even on continuous usage. Similarly the chemical durability of the resin matrix was tested using acid concentrations up to 4 M HCl. And it was found that the capacity of the resin to extent of the analyte did not decrease sufficiently even under high acidic conditions, thus providing its high chemical stability.



#### 4.10.6. Analytical results

The accuracy of the procedure was assessed by the analysis of three different concentrations of spiked solutions. And these standard solutions were prepared as recommended procedures and passed through the column with optimal conditions. Table IV-8 summarizes the results of replicate analyses, which are well within the 99% confidence limits.

Table IV-8: Recovery of Cu from the spiked water samples.

Conc. ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery %	RSD
10	9.91	99.1	3.28
20	19.85	99.25	3.15
40	39.58	98.95	3.24
		99.1	

#### 4.10.7. Effect of matrix ions:

The effect of interfering ions on the determination of Cu using column adsorption studies with functionalized triazine-AXAD-16 was investigated. The results are presented in Table IV-10. These are the concentration limits that caused less than 2 % error on recovery percentage. The results indicate that most of the anions and cations do not interfere in the determination of Cu by SPE method.

#### 4.10.8. Application of the method to real samples

Different water samples namely sea water, river water and ground water are collected and the determination of Cu in the sample was carried out by the present method. The results are presented in Table V-11. The results showed good agreement with the previously reported results [38, 39].

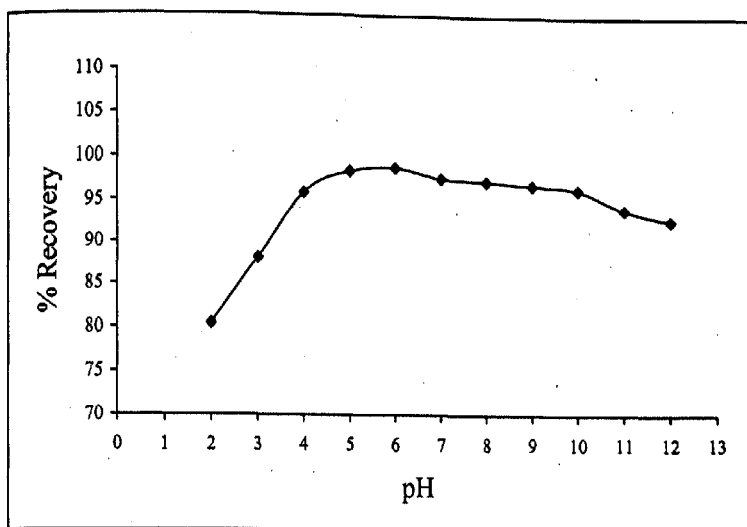


Figure IV-33: Effect of pH on the SPE determination of Cu

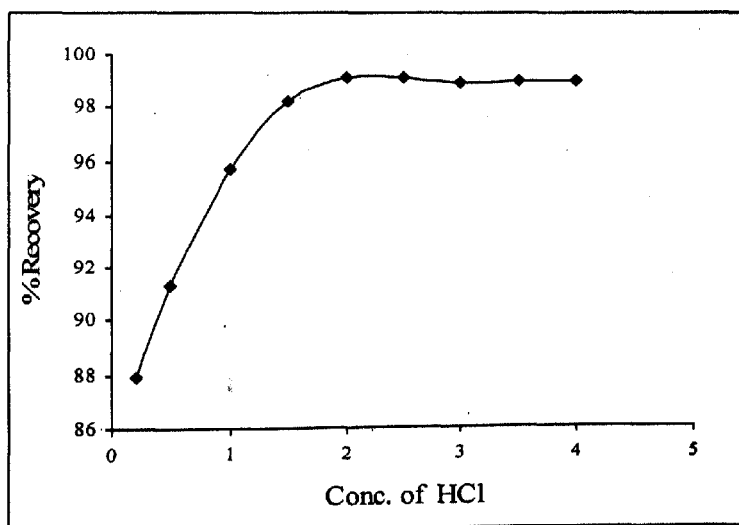


Figure IV-34: Effect of eluent Concentration on the SPE determination of Cu

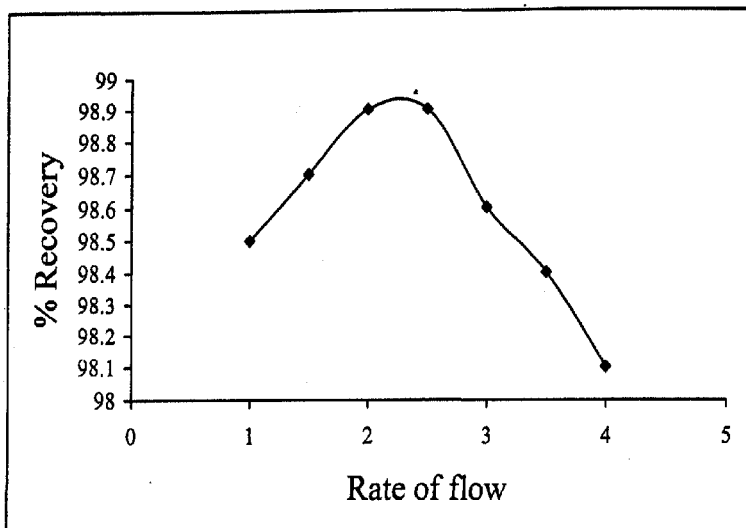


Figure IV-35(a): Effect of rate of flow of sample solution for the SPE determination of Cu

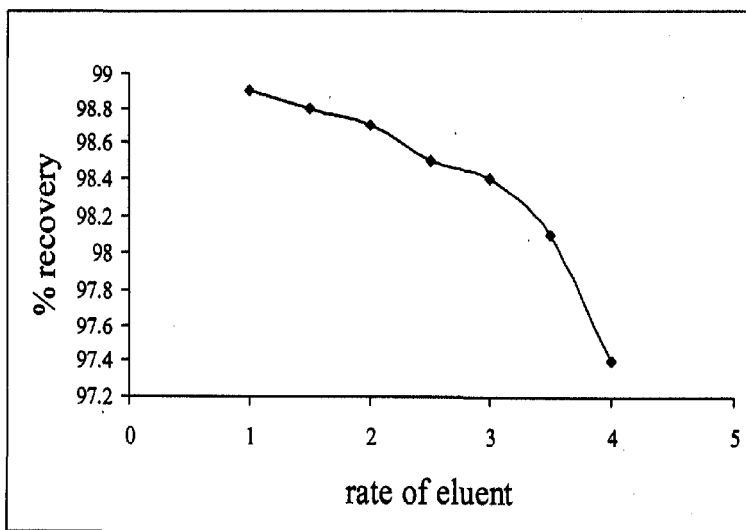


Figure IV-35(b): Effect of rate of eluent (2M HCl) on the SPE determination of Cu

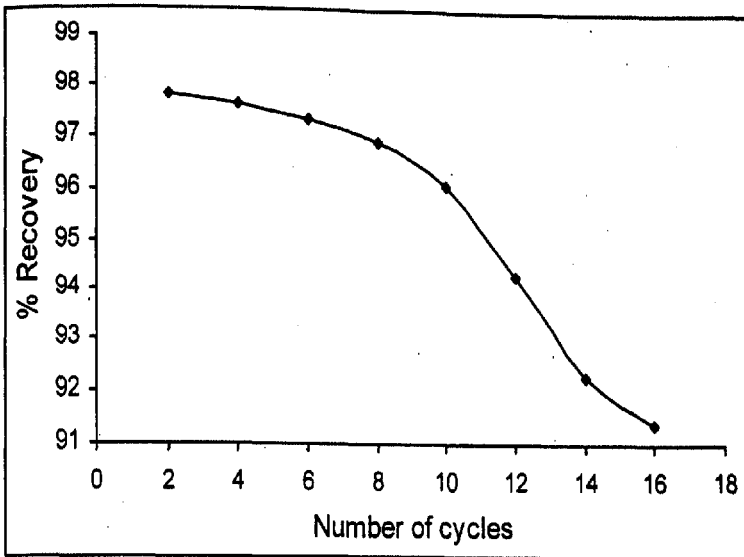


Figure IV-36: Graph to show the reusability of functionalized AXAD-16 for the determination of Cu by SPE

Table IV-9: Optimum conditions for the sorption and desorption of Cu ions

Experimental parameters		
pH range	5-6	5.5
Flow rate (ml/min)	1-4	2
HCl concentration for desorption <sup>a</sup> (M)	2-2.5	2
Sorption capacity of resin (mmol/g)	0.157	
Average recovery (%)	99.12	
Standard deviation <sup>b</sup>	0.01754	
Relative standard deviation (%)	3.22	

<sup>a</sup>Only HCl was used for desorption.

<sup>b</sup>For four determinations of 0.25 mg/mL metal ion

Table IV-10: Tolerance limits of matrix ions for the determination of Cu ions.

Foreign Species	Tolerance limit
NaNO <sub>3</sub> <sup>a</sup>	0.009
NaCl <sup>a</sup>	0.04
NaBr <sup>a</sup>	0.034
Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	0.009
Na <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	0.43
Ascorbicacid <sup>b</sup>	0.09
Citricacid <sup>b</sup>	2.2
EDTA <sup>b</sup>	0.24
Tartaricacid <sup>b</sup>	0.09
Ca(II) <sup>a</sup>	0.42
Mg(II) <sup>a</sup>	0.3
Mn(II), Ni(II) <sup>b</sup>	1.9
Zn(II), Pb(II), Cd(II) <sup>b</sup>	2.4

<sup>a</sup> = M/L. and <sup>b</sup> = mM/L

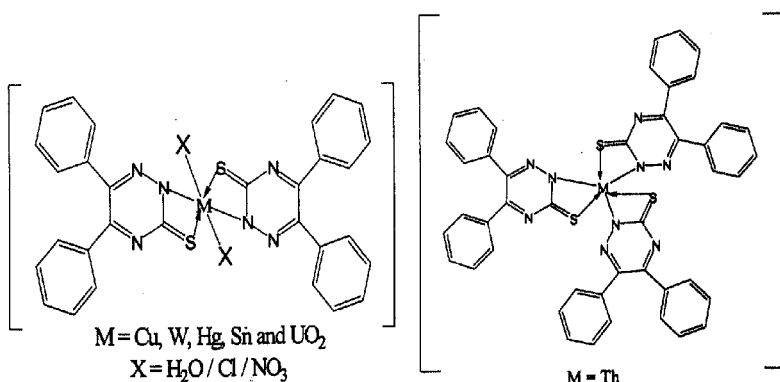
Table IV-11: Determination of Cu ions from real samples

Water sample	Amount of copper Found ( $\mu\text{g} / \text{L}$ )
Sea water	17.54
Ground water	21.43
River water	20.71

#### 4.11. Conclusion

Studies on the 5,6-Diphenyl-2H-[1,2,4]triazine-3-thione (triazine) metal complexes of copper, mercury, tin, tungsten, thorium and uranium are presented in this chapter. The IR, NMR, Mass and electronic spectral characterization and TG/DTA studies of the complexes are discussed. An XPS spectrum of copper triazine complex is presented to determine copper oxidation state in complex. The results showed that the triazine is a bidentate ligand and coordinates with all the studied metal ions through nitrogen and sulphur. The elemental analysis results showed that the complexes are in 1:2 stoichiometry (except thorium triazine complex which is in 1:3 stoichiometry). All the prepared complexes are coloured and conductivity measurements revealed that they are non electrolytic in nature. Magnetic susceptibilities and spectral studies indicated that the complexes are in octahedral geometry. Stability constants of the triazine metal complexes are carried out using potentiometric (Irving-Rosseotti) method and Gibb's free energy values are also calculated.

Based on the analytical, spectral investigations and magnetic susceptibilities the proposed structure of the metal flavonoid complexes are given below.



Based on the stability and solubility studies of the triazine complexes the analytical application of triazine for the quantitative determination of metals is studied. Results showed that the reagent could be successfully employed for solid phase extraction and determination of copper in various matrices.

The proposed method is simple and offers the advantages of high pre-concentration factor and good sorption capacities using AXAD-16 functionalized triazine for the determination of copper. The proposed method could be used as an alternative method for the determination of trace amounts of copper in various environmental samples.

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