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C H A P T E R - I

ANALYTICAL ASPECTS OF THIOSEMI CARBAZONE

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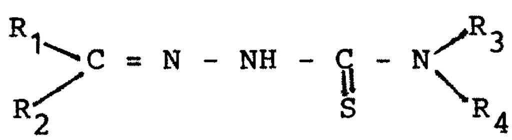
Introduction :

Thiosemicarbazones (TSC) and Semicarbazones are the class of the compounds, obtained by condensing thiosemicarbazide or Semicarbazide with suitable aldehydes or ketones. The active grouping for Chelation is shown below in structure(I)



(I)

Thiosemicarbazones and Semicarbazones act as chelating agents for metal ions by bonding through the sulphur atom with possible further coordination by hydrazine nitrogen atom to give five member ring. In a few cases they behave as unidentate ligands by bonding only through sulphur or oxygen atom.

Domagk et. al[1] reported for the first time the anti-tubercular activities of metal thiosemicarbazones. Since then a number of papers have been appeared on the pharmacology of this compounds. The metal TSC complexes were found to be active against influenza[2], protozoa[3], smallpox[4] and certain kinds of tumours[5] and to be very good pesticides[6] and fungicides[7]. The activity of TSC is thought to be due to their power of chelation with traces of metal ions present in biological systems.

The anti-tubercular activity of P-acetamidobenzaldehyde thiosemicarbazones is found to be enhanced by the presence of small amounts of copper ions[8].

Depending upon the type of aldehyde or ketone used for condensation, TSC and SC can act as unidendate, bidentate or multi dentate chelating agents for metal ions, producing highly coloured complexes. These coloured complexes are then used in selective and sensitive determination of metal ions. The aim of this review is to summarize these analytical applications.

Preparation of the Reagents :

Semicarbazones are obtained by condensing semicarbazide hydrochloride With suitable aldehyde or ketones in presence of sodium acetate. Some times hydrochloric acid must be present in the preparation of semicarbazones[9].

Thiosemicarbazones are prepared by condensing thiosemicarbazide with an aldehyde or ketone in the presence of a few drops of glacial acetic acid. Preparation of the mono derivatives is simple but the di-derivatives are a little difficult and require special treatment.

Dipyridylglyoxal dithiosemicarbazone[10] was prepared by cyclizing the monoderivatives with 6 M hydrochloric acid.

Chemical Properties :

Just as hydrazones are weaker bases than hydrazines, semicarbazones and thiosemicarbazones are weaker bases than semicarbazides and thiosemicarbazides respectively. Hydrolysis of these compounds yields first the hydrazones hence these compounds resemble hydrazones in many of their reactions.

Mild reductions of semicarbazones and thiosemicarbazones yield 1-substituted semicarbazide and thiosemicarbazide respectively. Catalytic reduction of these compounds yields hydrazides are further hydrolysed to hydrazines. Reactions with alkoxides such as sodium ethoxide converts semicarbazones into hydrazones and with a strong base, hydrocarbons are obtained. This reaction may be applied for replacement of the carbonyl group by a $-CH_2$ group.

Analytical applications :

Analytical applications :

The various thiosemicarbazones and semicarbazones which have been used as analytical reagents are summarized in Table-1.

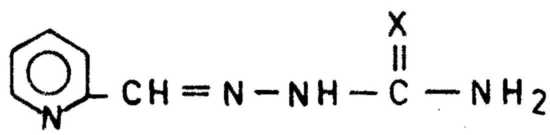
Table-1

Abbreviation	Structure	Systematic name	References
PAT	II	Picolinaldehyde thiosemi-carbazone	12-16
PAS	II	Picolinaldehyde semi-carbazone	17
DPGT	III	Dipyridyl glyoxal dithiosemicarbazone	10,18,19
DPKT	IV	Di-2-pyridyl ketone thiosemicarbazone	20
MPKT	V	Methyl-2-pyridyl ketone thiosemicarbazone	21
PAPT	VI	Picolinaldehyde-4-phenyl-3-thiosemicarbazone	22,23
APPT	VII	2-Acetylpyridine-4-phenyl-3-thiosemicarbazone	24
MPAT	VIII	6-Methylpicolinaldehyde thiosemicarbazone	25,26
HPAT	IX	3-Hydroxypicolinaldehyde thiosemicarbazone	27
GDT	X	Glyoxal dithiosemicarbazone	28
APT	XI	Acetophenone thiosemi-carbazone	29
HMAPS	XII	2-Hydroxy-5-methylaceto-phenone semicarbazone	30,31
HMAPT	XII	2-Hydroxy-5-methylaceto-phenone thiosemicarbazone	30,32,33
DAPT	XIII	2,4-Dehydroxyacetophenone thiosemicarbazone	34
BAMOS	XIV	Biacetyl monoxime semi-carbazone	17
BAMOT	XIV	Biacetyl monoxime thiosemicarbazone	35-39

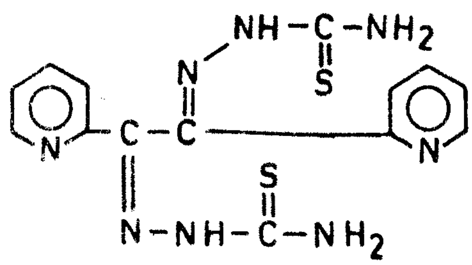
Abbreviation	Structure	Systematic name	References
BAMOPT	IX	Biacetyl monoxime 4-phenyl-3-thiosemicarbazone	40
BAMT	XVI	Biacetyl monothiosemicarbazone	41
DBAS	XVII	2,4-Dihydroxybenzaldehyde semicarbazone	42
DBAT	XVII	2,4-Dihydroxybenzaldehyde thiosemicarbazone	43-45
NBAT	XVIII	4-Nitrobenzaldehyde thiosemicarbazone	46
AMBAT	XVIII	4-Acetamidobenzaldehyde thiosemicarbazone	46
DABAT	XVIII	4-Dimethylaminobenzaldehyde thiosemicarbazone	47
ESBAT	XVIII	p-Ethylsulphonylbenzaldehyde thiosemicarbazone	48-50
SAS	XIX	Salicylaldehyde semicarbazone	51
SAT	XIX	Salicylaldehyde thiosemicarbazone	52-54
HNAT	XX	2-Hydroxy-1-naphthaldehyde thiosemicarbazone	55-56
TAS	XXI	o-Thymolaldosemicarbazone	57
TAT	XXII	Thiophene-2-aldehyde thiosemicarbazone	58
PADT	XXIII	a-Phthalaldehyde dithiosemicarbazone	59
PIDT	XXIV	Phthalimide dithiosemicarbazone	60-62
FAT	XXV	2-Furaldehyde thiosemicarbazone	63
NFAS	XXVI	5-Nitro-2-furaldehyde semicarbazone	64,65

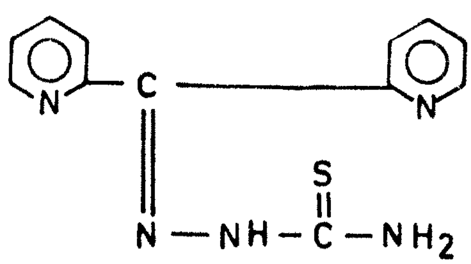
Abbre-viation	Stru-cture	Systematic name	References
PTFA	XXVII	4-Phenyl-3-thiosemicarbazone of 2-furaldehyde	66
NOT-4S	XXVIII	1,2-Naphthoquinone-2-thiosemi-carbazone-4-sulphonic acid	9,67 70
NQS-4S	XXVIII	1,2-Naphthoquinone-2-semi-carbazone-4-sulphonic acid	67 68,69,71
PQMT	XXIX	Phenanthrequinone monothio-semicarbazone	72
SAPT	XXX	Salicylaldehyde-4-phenyl-3-thiosemicarbazone	73
1,2CDDT	XXXI	1,2-Cyclohexanedione dithio-semicarbazone	74,75
1,3CDDT	XXXII	1,3-Cyclohexanedione dithio-semicarbazone	76
FACT	XXXIII	Furylacrolein thiosemicarbazone when R = 2-furyl and R' = H R = Ph,2-furyl,5-methyl-2-furyl,5-nitro-2-furyl and R = H, Et	77,78
TBPK	XXXIV	2-Benzothiazolylphenyl ketone thiosemicarbazone	79
IT	XXXV	β-Ionone thiosemicarbazone	80
BTDD	XXXVI	Bisthiosemicarbazone of diethyl-3,4-dioxadioate	81
LS	XXXVII	Lawsone semicarbazone	82
FPDT	XXXVIII	Furylpentadienal thio-semicarbazone	83

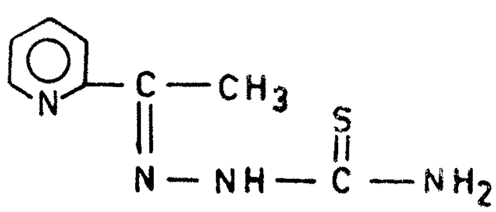
Thiosemicarbazones and Semicarbazones.

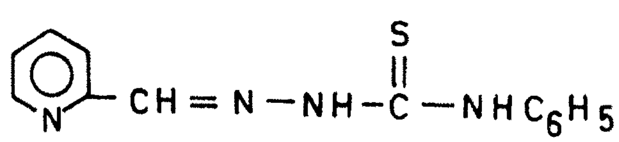
(II) 

When X=S.PAT
X =O.PAS

(III) 

(IV) 

(V) 

(VI) 

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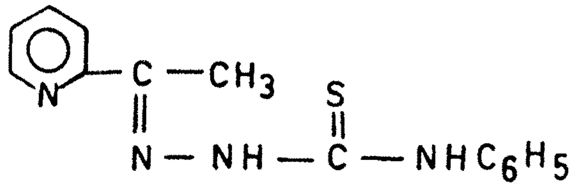

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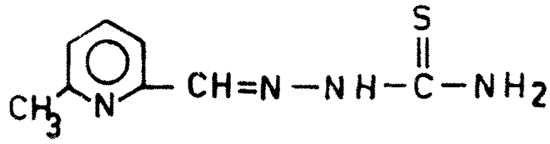

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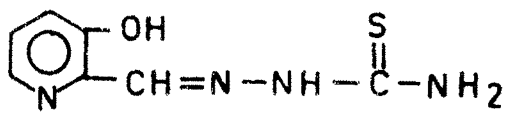

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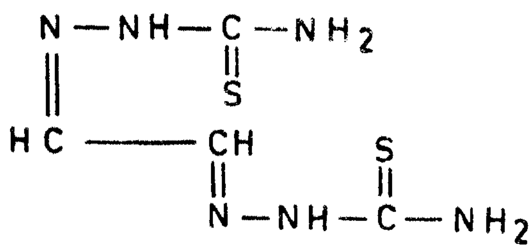

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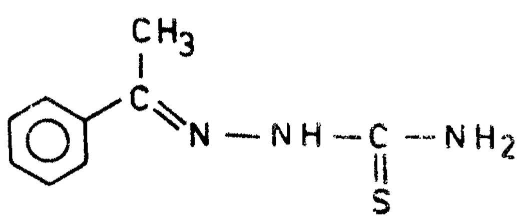

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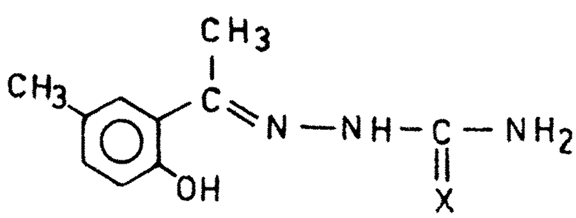
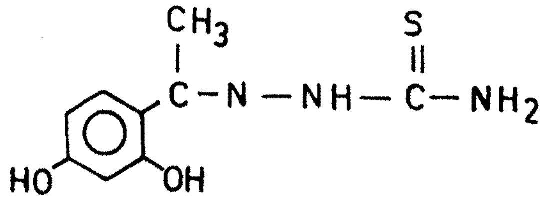


When X=O·HMAPS
X=S·HMAPT

(XIII)



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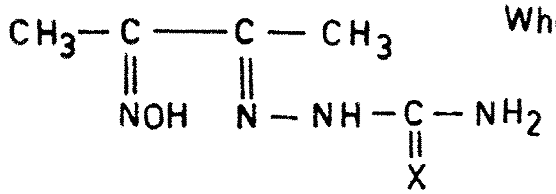
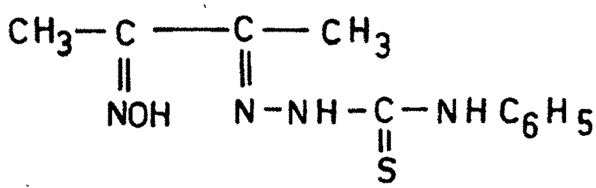


When X=O.BAMOS

X=S.BAMOT

(XV)



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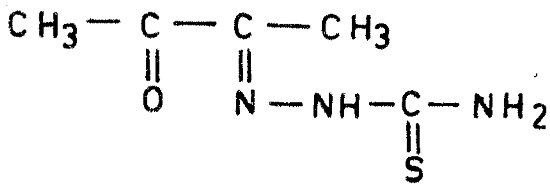

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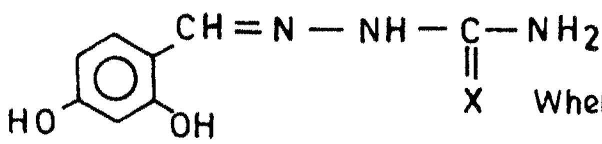


When X=O·DBAS

X=S·DBAT

(XVIII)

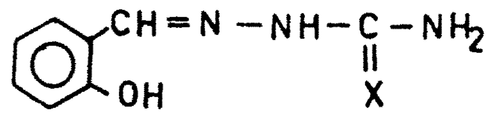
When $Y=NO_2$, NBAT

$Y= -CH_2CONH$, AMBAT

$Y= N(Me)_2$, DABAT

$Y= SO_2Et$, ESBAT

(XIX)



When X = O, SAS
X = S, SAT

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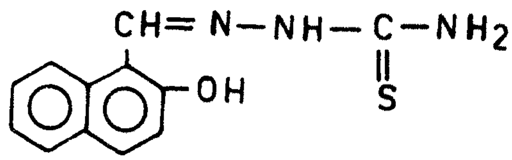

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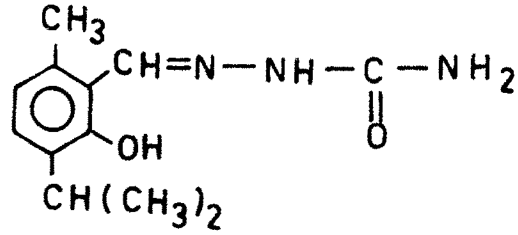

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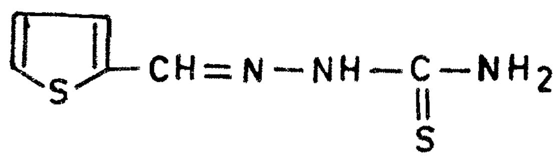

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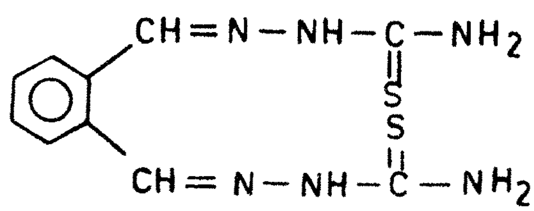

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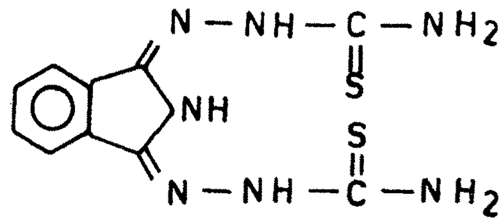

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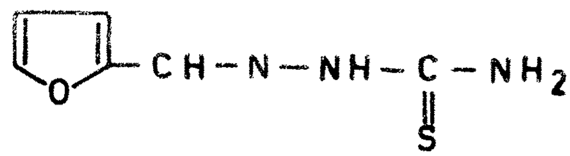

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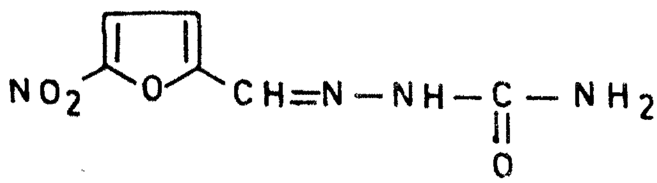

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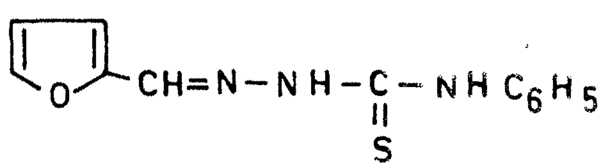

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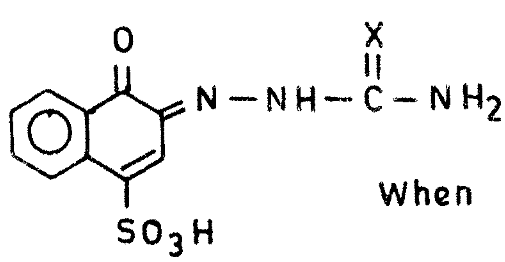
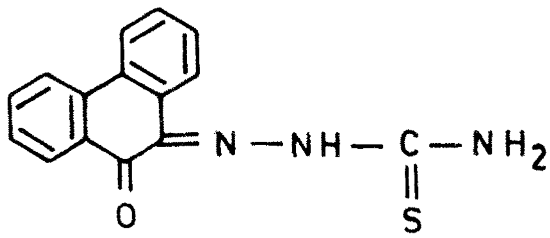


When X = S·NQT-4S

X = O, NQS-4S

(XXIX)



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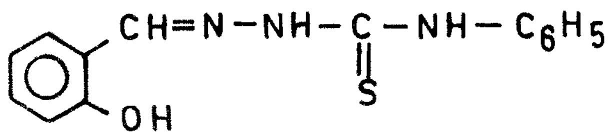

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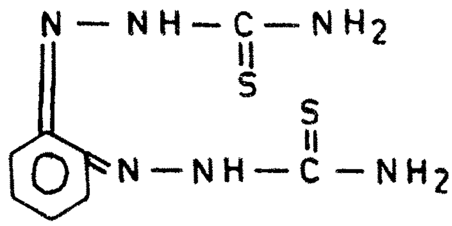

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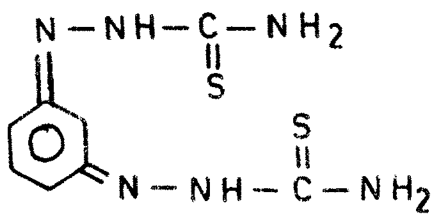

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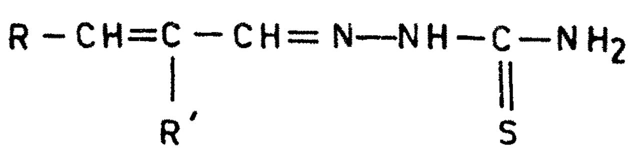

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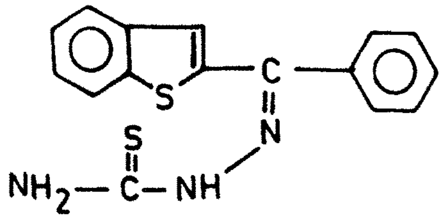

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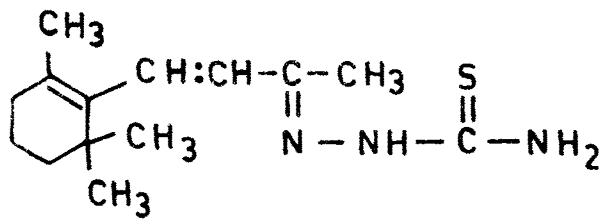

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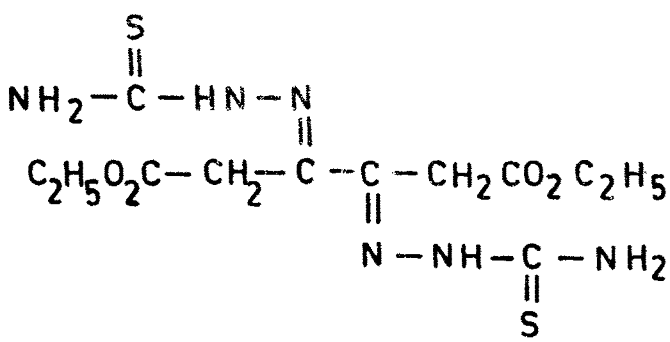

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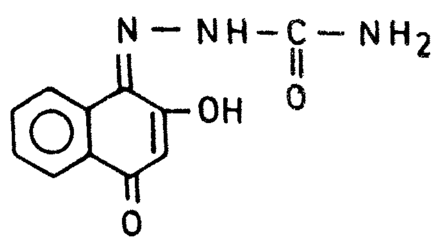

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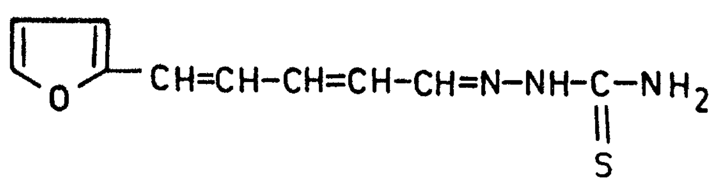

Applications in Spectroscopy :

Semicarbazones and thiosemicarbazones from Coloured Metal Complexes in condition ranging from moderately alkaline. Only a few are used to determine metal ions in highly acidic medium. 3-Hydroxypicolinaldehyde thiosemicarbazone is used to determine Co(II) in highly acidic medium[27]. Similarly glyoxal dithiosemicarbazone reacts with Ag(I) and Hg(II) at pH 1.1[28]. Salicylaldehyde thiosemicarbazone has been used to determine Mo(VI) in presence of iron in highly acidic medium[2].

Extraction of the complexes not only increases the sensitivity but is also helpful in simultaneous determination of metal ions. Dipyridylglyoxal dithiosemicarbazone[19] reacts with Ni(II) and Co(II) at pH 5.2, but only the Ni(II). Complex is extractable into chloroform, and hence allows the determination of both metals when present together. Biacetyl monoxime thiosemicarbazones has been used to determine Bi(III) in presence of Cu(II) by extraction of the complex into isobytyl methyl ketone[38]. Presence of EDTA[15,18,28]is sometimes necessary for completion. Cyclohexane 1-2 dione dithiosemicarbazone has been used to determine Cu(II) in alkaline medium, alkaline tartrate medium and EDTA medium[84]. It was generally observed that semicarbazones containing hydroxy groups ortho to the aldehyde groups gave good colour reactions. Thiosemicarbazones are rather selective and sensitive for copper.

Applications of these compounds for spectrometric investigations are summarized in following paragraphs.

Applications in Visual Indicators :

The most common applications is the direct titration of the metal against EDTA solution with thiosemicarbazones and semicarbazones as indicators with O-thymolaldosemicarbazones[57], addition of acid of alkali has no effect on the complex formed. Phenanthraquinone monothiosemicarbazone[72] was used to determine Cu in brass and gun metal, and Ni in monel K and Brightway G. phosphate molybdate, tungstate and sulphate were titrated with lead nitrate with 1,2 naphthoquinone, 2-thiosemicarbazone-4-sulphonic acid as indicator and zinc solution as titrant[69]. Aluminium and copper were determined together by breaking the Al-EDTA complex by addition of sodium flouride and titrating the released EDTA with zinc[69]. Iodide has been determined by mercurimetric titration in isopyropyl alcohol, with the same indicators[67].

Applications as gravimetric reagents :

Only a very few semicarbazones and thiosemicarbazones are used in the gravimetric determination of metal ions. Komatsu and Hiroaki used a 0.1% ethanolic solution of P-ethylsulphonyl benzaldehyde thiosemicarbazones for gravimetric determination of Hg^{+2} in acidic medium (2.5 N)[49].

It gives a yellow precipitate which is washed with 1 M hydrochloric acid and dried at 110-120^{o}. It is also used for estimation of Pd(II)[50] giving an orange yellow precipitate in 5 M hydrochloric acid, which is washed with 1% hydrochloric acid and water and dried at 110–120°. Hovorka and Holzbecker[54] used salicylaldehyde thiosemicarbazone to precipitate the yellow crystalline $Cd(C_8H_8ON_3S)_2$ (containing 22.4% Cd) from cadmium nitrate or sulphate solution the method is not applicable to solution containing chloride, fluoride or oxalate.

2,4-Dihydroxybenzaldehyde thiosemicarbazone has also been employed for estimation of cadmium[44] and nickel[45]. In the cadmium estimatiion of pH 6.5 - 8.5, Fe^{+3}, Al^{+3}, Cr^{+3}, CN^-, Citrate, traces of F^- and 2.5 mg/ml of other halides interfere. In the estimation of nickel, the green complex $(C_8H_8N_3O_2S)_2$ Ni. $6H_2O$ was precipitated in the pH range 5.0–6.5. 2 Furaldehyde thiosemicarbazones has been used by Pavon and Pino[63] as a gravimetric reagent, for palladium at pH 2.0-6.0. The orange precipitate is washed with 10% aqueous ethanol and dried at 60-120°. The reagent is said to have advantages over dimethyl glyoxime and 2-furaldioxime.

The same authors[66] used a 2% ethanolic solutions of the 4 phenyl 3-thiosemicarbazones of 2-4 furaldehyde for gravimetric estimation of palladium in the pH range 3.0-5.0.

Potentiometric Studies :

Bhatt et. al[55] studied the complexes of 2-hydroxy-1-naphthaldehyde 4-phenyl-3-thiosemicarbazone with Cu^{+2}, Ni^{+2}, Co^{+2} and Vo^{+2} by pH titrations. The proton ligand stability constant is 1.43×10^{10}. The stability constants were determined by several methods in 70% dioxan medium. All four metals formed 1:2 complexes. The order of the stability constant is $Vo^{+2} > Cu^{+2} \simeq Co^{+2} > Ni^{+2}$.

Complexation by salicylaldehyde 4-phenyl-3-thiosemicarbazone has also been studied potentiometrically by Bhatt et. al[73] at 25^{o} and ionic strength 0.1 in 50% aqueous dioxan. The proton ligand stability constant is 7.94×10^{9} and the log β values for the complexes are 9.44, 10.28, 9.84, and 8.94 for Vo^{+2}, Cu^{+2}, Co^{+2} and Ni^{+2} respectively.

Similar studies were done on the 2-hydroxy-5-methyl aceto phenone thiosemicarbazone complexes[33] of Cu(II), Mn(II), Co(II), Zn(II) and Ni(II) at 40^{o} in water dioxan (1:3). The order of the stability constants is Zn $<$ Cu $>$ Co $>$ Ni.

Fluorimetric determination :

Salicylaldehyde semicarbazone 2-hydroxy-1 naphthaldehyde thiosemicarbazone and 2-4 dihydroxybenzaldehyde semicarbazone have also been used for the spectro fluorimetric determination of a number of metal ions.

<u>Other Uses</u> :

In the presence of cynide and tartrate manganese can be detected by a spot test on the paper even when Ag, Pb, Cu, Cd, Bi, Ni, Zn and Fe(III) are present by use of an ethanolic solution of dimethylglyoxime thiosemicarbazone. Complexes of Cu(II), Hg(II), Cd(II) and Zn(II) with the 4,4' diphenyl thiosemicarbazones of 1,2 diketones can be separated by thin-layer chromatography on alumina with ethyl acetate as solvent.

The literature survey has revealed that 6-methyl, 2-Chloro quinoline 3-carbaldehyde, thiosemicarbazone has not been used for spectrophotometric determination of Cobalt, Iron, Nickel. Hence the present work centers around the synthesis and applications of this reagent in spectrometric determination of Co(II), Fe(III) and Ni(II).

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