CHAPTER-II

CHEMISTRY OF DITHIOCARBAMATES
The development of the concept of coordination theory by the Switzerland Noble Prize awardee, Werner\textsuperscript{1} in 1893 revolutionized the approach to the structure of inorganic compounds and permitted the entire area of coordination chemistry. Since then number of ligands have been introduced in inorganic analysis because of their selectivity and sensitivity. Dimethyl-glyoxime is an example of such organic reagents in which it is highly selective for Ni(II)\textsuperscript{2}. Organic analytical reagents are found to be advantageous than inorganic reagents for their reactivity, sensitivity and selectivity and voluminous literature is available on their use\textsuperscript{3-5}. The separation of metal ions are simple and more effective with the organic reagents and hence they have several applications in gravimetric, titrimetric and spectrophotometric determinations and as masking and demasking agents in certain extractive separations of metals\textsuperscript{6-9}. Of the various organic reagents, thio compounds have a favoured position because of the ease of replacement of H\textsuperscript{+} from \(-\text{SH}\) group which leads to the formation of coloured complexes with coordinate bonds through S-atom with transition metal ions. Dithiols, Xanthates and Dithiocarbamates are some of the thio compounds, extensively used in inorganic analysis.

\textbf{II.1. Dithiocarbamates:}

The dithiocarbamates, as a class of chemical compounds, are discovered early in the history of organo-sulfur chemistry and are the half amides of dithiocarbamic acid. The simplest way of synthesis of these compounds is as follows:
N-substituted dithiocarbamic acids, RNHCSNH or R₂NCSSSH are formed as their substituted ammonium salts by reaction of CS₂ with a primary or secondary amine, usually in alcoholic \(^{10}\) or aqueous solution \(^{11}\). More valuable amine compounds of dithiocarbamates are prepared by using alkali metal hydroxide.

\[
\text{RNH}_2 + \text{CS}_2 + \text{NaOH} \rightarrow \text{RNH} \text{CSSNa} + \text{H}_2\text{O}
\]

The sodium or ammonium salts of dithiocarbamates are sufficiently stable than the corresponding carbamic acids. Sodium salts of dithiocarbamates are white crystalline solids freely soluble in water. The salts are stable over a long period but the solutions of dithiocarbamates are to be prepared freshly whenever required.

Most of the heavy metal compounds of the dithiocarbamates are coloured, facilitating spectrophotometric methods in Visible or near UV region. They are prepared simply by the addition of a solution of the heavy metal ion as its chloride, sulphate, etc., to a solution of an ammonium or alkali metal salt of the dithiocarbamic acid \(^{16}\). Heavy metal compounds are sparingly soluble in water, being more soluble in organic solvents such as chloroform, carbon tetrachloride and ethyl ether.

Dithiocarbamates are decomposed in acid solutions. The breakdown of dithiocarbamic acid into amine and CS₂ in the presence of mineral acids has been used as the basis for quantitative estimation of dithiocarbamates \(^{17}\). The liberated CS₂ can be estimated by iodometry as the amount of liberated CS₂ is directly proportional to the concentration of dithiocarbamate.
The detailed study\textsuperscript{12-15} of various dithiocarbamates and their derivatives through infra red spectra confirms the contribution of various forms equally to the structure. The significant among several canonical forms for the dithiocarbamates in their metal complexes, M(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{n} are as follows:

### II.1.1 Physico Chemical Concepts of Dithiocarbamates:

\[
\begin{align*}
\text{I (a)} & : \quad \text{M} - \text{S} \quad \text{S} \quad \text{C} = \text{NR}\textsubscript{2} \\
\text{I (b)} & : \quad \text{M} - \text{S} \quad \text{S} \quad \text{C-NR}\textsubscript{2} \\
\text{I (c)} & : \quad \text{M} - \text{S} \quad \text{S} \quad \text{C-NR}\textsubscript{2}
\end{align*}
\]

where M is a metal atom and n is its valency. Although these forms contribute equally to all the structures of all N, N-dialkyl dithiocarbamic acid derivatives, the canonical form I(a) arises from the mesomeric electron releasing tendency of the R\textsubscript{2}N-group. By this electron drift into the sulphur atoms not only the electron donor capacity increased but the formation tendency of strong complexes with the heavy metals also enriched with reducing tendency of forming dative \Pi bonds between the metal and sulphur atoms.

### II.1.2. Properties:

Ammonium salt of dithiocarbamates is white or light yellow crystalline solid, which is freely soluble in water. The salts are stable for long period and the solutions of dithiocarbamates may be prepared freshly whenever required.
II.1.3. Analysis of dithiocarbamates:

The breakdown of dithiocarbamic acids into amine and CS$_2$ in the presence of mineral acid has been used as the basis for the quantitative estimation of dithiocarbamates. The liberation of CS$_2$ can be estimated by iodometry. The amount of liberated CS$_2$ is directly proportional to the concentration of dithiocarbamate. The applications of dithiocarbamates are found in various fields of science.

II.1.4. Applications in Agriculture:

The fungicidal activity of dithiocarbamates was described by Martin$^{18}$, and Tisdale and Williams$^{19}$. These compounds are hailed as all purpose fungicides, and recommended in soil treatment, seed treatment and foliar sprays for the control of a great variety of diseases of a large number of crops$^{20}$. Thiuram is outstanding among the dithiocarbamates as a seed treatment material$^{21,22}$. Their use as insecticides$^{23,24}$ herbicides$^{25}$, bacteriosides and microbicides$^{26}$ are noteworthy. The nitrogen derivatives of dithiocarbamic acids have been found to have wide applications and a vast amount of work has been published in biological activity and fungicidal action$^{27}$. DTCs were first introduced as fungicides for commercial applications during World War II (Ware & Whicare, 2004)$^{28}$.

In addition to these applications dithiocarbamates also find extensive use in industry as vulcanization accelerators, in the field of rubber chemistry$^{29,30}$, electroplating$^{31}$, in hardening of resins$^{32}$, as catalysts$^{33}$ etc.

Because of their biological activity they have more practical value and applications in the fields of Medicine and Agriculture.
II.1.5. Applications in Clinical Medicine:

Research over the past half a century has amply demonstrated that the dithiocarbamates have a profound effect on biological systems. They have been extensively used as inhibitors in research on enzymes, as antifungal, antibacterial agents\textsuperscript{34,35}, as antituberculostatic agents\textsuperscript{36,37}, as biocidal agents\textsuperscript{38} in the treatment of skin diseases\textsuperscript{39}, in control of various dermatophytes\textsuperscript{40}, in the treatment of chronic alcoholism\textsuperscript{41}, as protective agents against the lethal effects of X-radiations\textsuperscript{42,43} and as prophylactic agents against radiation of sickness\textsuperscript{44}. Tetramethyl thiuram disulphide is one such compound that has greater medicinal value in controlling various dermatophytes, treating scabies and correcting chronic alcoholism. Because of its medicinal importance it is used as an ingredient in various soaps and lotions. Similarly these compounds have played a major role in rubber chemistry, as vulcanization accelerators and antioxidants.

II.1.6. Analytical applications of dithiocarbamates:

In addition, these carbamates have also played a major role and found an unique place in analytical chemistry as reagents for metal ions\textsuperscript{45-47} due to their metal binding property and chelating tendency. Since the research on dithiocarbamates has been revealing some promising new avenues in all fields of sciences, including inorganic analysis, the inclusion of all the references is beyond the scope of this dissertation. Attention has therefore, been paid to incorporate the various dithiocarbamates used for spectrophotometric determination of metal ions\textsuperscript{48-258} in the consolidated form in the table. However, an emphasis is made to include a detailed account of various dithiocarbamates used for the determination of metal ions which are analysed in the present study in the respective sections.
### Various dithiocarbamates used in the analysis of metal ions

<table>
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<th>S.No</th>
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<td>Triethylammonium cyclohexyl</td>
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<td>benzyl dithiocarbamate</td>
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<td>Tetramethylenedithiocarbamate</td>
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<td>26</td>
<td>Copper diethyl dithiocarbamate</td>
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<td>Be 65</td>
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<td></td>
<td></td>
<td>Ag 248</td>
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### Chemistry of Dithiocarbamates

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<td>29</td>
<td>Potassium dicarboxymethyl-</td>
<td>Cu</td>
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<tr>
<td></td>
<td>dithiocarbamate</td>
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<tr>
<td>32</td>
<td>Pentamethylene dithiocarbamate</td>
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<td>(PipDTC)</td>
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<tr>
<td></td>
<td></td>
<td>metal ions</td>
<td>249 – 255</td>
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</table>

The table shows the various dithiocarbamates used extensively for the spectrophotometric analysis of a number of metal ions. Of these the application of Pentamethylene dithiocarbamate as an analytical reagent has been mostly using different techniques such as amperometry\textsuperscript{256}, pHmetry\textsuperscript{258,259}, Spectrophotometry\textsuperscript{50-255,260} and catalytic polarography\textsuperscript{257}.

### II.1.7. Determination of trace metal ions using morpholine dithiocarbamate by different techniques:

Differential pulse polarographic analysis of trace amounts of vanadium and molybdenum in various standard alloys and environmental samples after pre-concentration of their morpholine-4-
carbodithioates on microcrystalline naphthalene or morpholine-4-dithiocarbamate, cetyl trimethyl ammonium, bromide - naphthalene adsorbent has been developed by Puri et al\textsuperscript{26}\textsuperscript{1}. Simultaneous determination of lead and cadmium in various environmental and biological samples by differential pulse polarography after adsorption of their morpholine-4-carbodithioates onto microcrystalline naphthalene or morpholine-4-dithiocarbamate-CTMAB-naphthalene adsorbent procedure was developed by Dubey and Puri\textsuperscript{26}\textsuperscript{2}.

Application of morpholine dithiocarbamate (MDTC) coated Amberlite XAD-4, for preconcentration of Cu(II), Cd(II), Zn(II), Pb(II), Ni(II) and Mn(II) by solid phase extraction and determination by inductively coupled plasma (ICP) atomic emission spectrometry (AES) was developed by Rao et al\textsuperscript{26}\textsuperscript{3}.

Rao et al\textsuperscript{26}\textsuperscript{4} developed a preconcentrated method by using Amberlite XAD-7 impregnated with morpholine dithiocarbamate (MDTC) for separation and determination of trace amounts of lead, copper, cobalt, iron, nickel, cadmium and zinc and by ICP-AES in various environmental samples. Todorovi et al\textsuperscript{26}\textsuperscript{5} employed preconcentration of trace metals in natural waters and model samples with standard metal concentrations by using 4-morpholine dithiocarbamate-complexes. The formed complexes were extracted with chloroform. Different methods for recovering the metals from the organic solvent were studied and compared with AAS metal analysis. The developed preconcentration method was successfully applied to the determination of trace metal concentrations in water samples.

A preconcentration system for the determination of cobalt in water was developed. The system studies uses a glass column packed with Amberlyst A-26 resin modified with ammonium morpholine
dithiocarbamate and analyzed by flame atomic absorption spectroscopy\textsuperscript{266}. A selective and sensitive derivative method for the simultaneous determination of trace amounts of Co(II) and Ni(II) with morpholine dithiocarbamate (MDTC) in the presence of sodium lauryl sulphate (SLS) was developed by Varinder Kaur et al\textsuperscript{267}. Dubey et al\textsuperscript{268} developed a highly selective, sensitive and rapid differential pulse polarographic method for the estimation of trace amounts of indium in standard alloy, ore, synthetic and environmental samples. The morpholine-4-dithiocarbamate of indium (III) is adsorbed on microcrystalline naphthalene in the pH range 3.5-6.4. The catalytic hydrogen waves of organic thio compounds in the presence of Cr(VI), Cr(III) and Mn(II) at DME in various environmental samples have been reported for the first time by Saraswathi and her associates\textsuperscript{269-278}. Catalytic hydrogen method was developed for the determination of Co(II) at DME in water samples, agricultural materials and pharmaceutical samples by Saraswathi et al\textsuperscript{279,280}. D.C polarographic technique with catalytic hydrogen wave was earlier developed in laboratories\textsuperscript{281-284} for the determination of Ni(II) in drinking water samples and agricultural samples. A catalytic polarographic method for the determination of microgram quantities of Cu(II) was developed based on the catalytic currents of copper in the presence of antipyrine in sodium perchlorate medium\textsuperscript{285}. Voltametric studies was developed for the investigation of Cu(II) in various environmental samples with Xanthates at DME by employing D.C. Polarography\textsuperscript{286}. Simple and sensitive catalytic hydrogen polarographic method was developed for the determination of chromium (VI) and catalytic hydrogen wave technique was developed for the analysis of manganese (II) with ammonium Piperidine dithiocarbamate and ammonium morpholine dithiocarbamate, respectively, in various water systems, leafy vegetables and medicinal plants by Kanchi\textsuperscript{292,293}. Spectrophotometric determination of cobalt and manganese with MDTC
in environmental samples was proposed by Saraswathi and Madhavi\textsuperscript{295,296}.

It is thought worthwhile therefore, to extend the application of the reagent to develop simple, sensitive and rapid spectrophotometric methods for some of the precious and environmentally toxic metal ions. These include silver (I), tin (II), selenium (IV), tellurium (IV), mercury (II) and determination of their levels in pharmaceuticals, biological and environmental samples.

**Advantages of (MDTC) as analytical reagent:**

1. Water of crystallization is not known in (MDTC) metal complexes and hence are easily extractable into organic solvents.

2. The metal complexes of the ligand are stable because of the contribution of the resonance hybrid structures.

3. The compound possesses high electric dipole moment.

4. The electron releasing tendency of N- group into sulphur atom increases the electron donor capacity of (MDTC) to give strong complexes with number of metal ions.
5. The preparation of the reagent is simple, easy and the time required is less than 45 minutes.

6. The precipitates of the metal complexes are extractable into commonly available solvents as chloroform and carbon tetrachloride and are stable in the solvent for sufficient time.
REFERENCES

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