ABSORPTION OF METAL IONS BY NATIVE AND MODIFIED NIGERIAN WOOL

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ABSTRACT

Wool and hair constitute a major component of effluent materials in the tanning industry. Since they are insoluble in aqueous medium where most of the tanning processes are undertaken, it becomes necessary to investigate other sources that will convert their insolubility into a useful process and cut down the cost of production

Conditioned native and modified Yankasa wool fibres were treated with metal ions and the uptake was measured. The effect of metal ion uptake on the mechanical properties of the wool was also determined. Yankasa wool fibres impregnated with metal ions were subjected to infrared spectroscopic studies. These studies showed that interaction between the reactive groups in wool (hydroxyl, amino,phenolic and carboxyl groups etc) and the electron dificient metal ions result in complex formation. As a result, Yankasa wool fibres which hitherto are drained into effluent tanks and later collected and burnt, can now serve as scavengers for retriving expensive and toxic metal ions from industrial water. Furthermore, the treatment has been found to improve the tensile strength, flexibility and modulus.

Chapter I

1.1 INTRODUCTION

Wool and hair are some of the animal by-products which presently lie wasted in this country when an animal is slauthtered or is dead by other causes. Wool is a major source of the keratins which are fibrous proteins of long chain molecules, aligned along the fibre.[1] Since wool is insoluble in aqueous medium, it constitutes a major component of effluent materials especially in leather processing operations. This insolubility, together with the presence of high reactive sites having affinity for ions, will make wool potentially useful as an insoluble matrix for removing both toxic and expensive metal ions by binding from aqueous solutions.

1.1.2 Function and source of Yankasa Wool

Wool grows on higher vertebrates as a protective covering, forming a barrier between the animal and its environment[2]. The main sources of wool in Nigeria are from the sheep Yankasa and Ouda located in the savanna regions around Kano, Kaduna, Gongola and Plateau states. It is estimated that between 2 to 2.4 million heads of sheep are produced yearly in the country.[3,4]

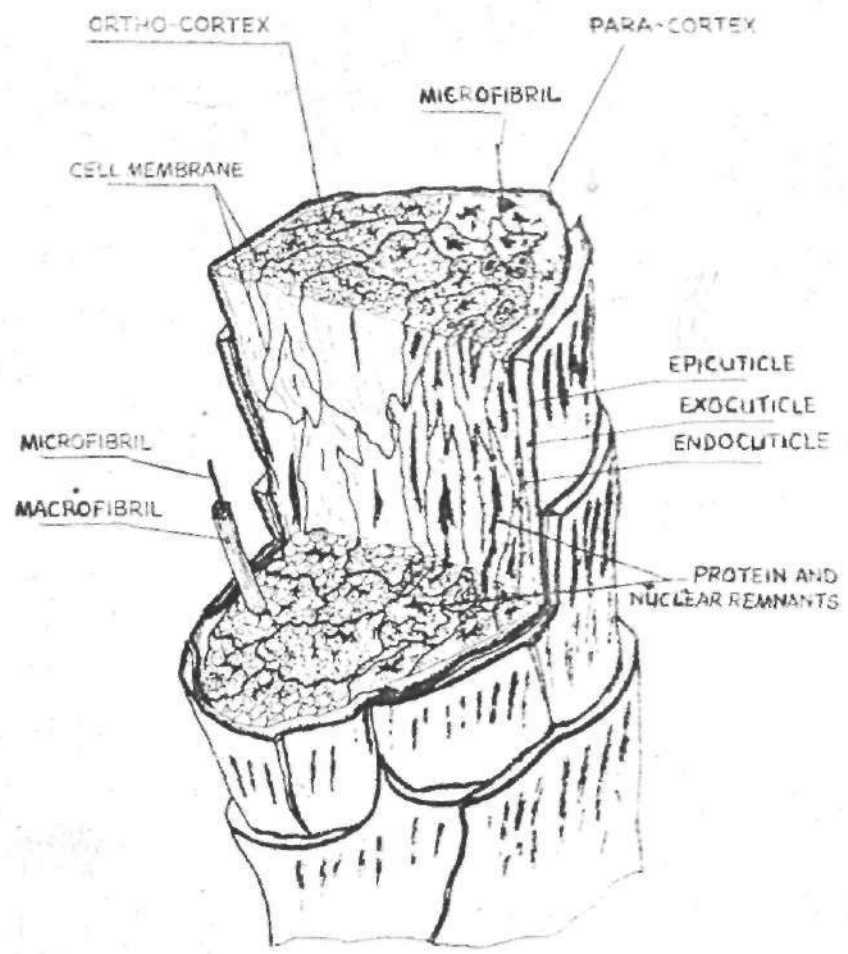


Fig. 1. *Diagram summarising the main features of the cuticle and cortex* [Ref. 1]

1.1.3 General structure of Wool fibre

The technique of electron microscopy[5] has shown that fine wool contains two types of cells, the flattened external cuticle cells and long polyhedral cortical cells, In coarse wool fibres such as Yankasa, there is a third cellular component, the medulla which forms a central core of interlocking cells. A diagramatic representation of wool structure is shown in fig. 1.

Cuticle

The cuticle in keratin fibres varies from one type to another and is present to about 2-10%in wool. Its consits of three layers - epicuticle, exocuticle, and endocuticle and overlap in the longitudinal direction of the fibre. X-ray, birefringence and electron microscopy studies by Hock[6], Hock and McMurdie[7] have shown that the cuticle is an amorphous protein. This has been confirmed by the fact that powdered wool and cortical cells show birefringence whereas cuticle does not. Zahn[8] has shown that the cuticle cells are separated from one another and the underlying cortex by longitudinal fibrils called the cell membrane complex similar to that which separates the cortical cells from one another. The cuticle is much less extensible than the cortex and swells less than the cortex, since longitudinal cracks are formed when fibres are swollen diametrically by greater than 30%. This results from the greater degree of cross-linking of the cuticle compared with the cortex, particularly the exocuticle where there is about one cross-link per five amino acid residue.

Appleyard and Greville[9] found that the cuticle of wool is normally one cell thick around the fibre except where cells overlap. This has been confirmed by Sikorski[10] and other workers who examined the cross sections and longitudinal sections by transmission electron microscopy. Large diameter-fibres like Yankasa tend to have multiple layers of cells in their cuticle and overlap both in the transverse and longitudinal direction amounting to about one sixth of the length of the cuticle cell.

The epicuticle

The epicuticle is a thin membrane which covers the external surface of keratin fibres and is the source of their hydrophobic nature.[11] King and Bradbury[12] have disproved that the epicuticle contains some carbohydrate but suggested that it is about 80% protein and 5% lipid. This view was independently confirmed by Lofts and Truter[13]. Leeder and Bradbury[14] showed that the epicuticle is a chemically resistant membranewhich completely surrounds each cuticle cell thereby preventing the egress of soluble polypeptides from the Allworden sac, through the underside of the separated cuticle cell. They therefore proposed that the epicuticle originated from the cell membrane complex of the cuticle cell[15].

The exocuticle

This is the cuticle layer which appears to be on the outside of the fibre, since the very thin epicuticle membrane on the surface is not visible.

It is generally considered to represent slightly more than half of the total cuticle cells, and Bradbury and Ley[16] have shown in a recent chemical study on merino wool that it occupies 64% of the cuticle.

The endocuticle

This is a well defined layer below the exocutice and separated from the next underlying cuticle cell by a cell membrane complex. Birbeck and Mercer[17] as well as Rogers[18], in their studies on developing hair fibres showed that the endocuticle consists of the cytoplasmic debris derived from the cytoplasm of the once living cuticle cell which is an intermicrofibrillar material.

The cell membrane complex which underlies the external cuticle cells and surrounds completely the internally situated cortical cells of the fibres, form a network structure which was identified by Appleyard and Dyncoke[19]. This complex carries out an important function of sticking the cells together, a function without which the cells would have fallen apart as is the case when the membrane complex is dissolved by enzymatic action[20] or when it is chemically treated with formic acid.

The Cortex

The cortex of keratin fibres contains a complex structure which by far outweighs that in the cuticle and cell membrane complex. It constitutes the largest proportion of the fibre and is up to 86.5% in fine wool. It is responsible for many of the physical properties of wool such as elasticity. The cortex is bilaterally segmented into two major components, now generally called orthocortex and paracortex.

The ortho and para cortices are approximate hemicylinders wound round each other helically in phase with the crimp of the fibre, so that the paracortex is always placed on the inside and the orthocortex on the outside of the crimp curvature. Early workers have shown that the orthocortex is more accessible and more readily dissolved than the paracortex.[22] Horio and Kondo[23] found that fibres which show bilateral asymmetry are crimped or curled, and those that are bilaterally asymmetric are relatively straight. Therefore, fine wool fibres are normally bilaterally asymmetric and crimped while crimpless mutant merino wool shows cylindrical asymmetry with a core of orthocortex.[24] As wool fibres become coarser, there is a transition from crimped, bilaterally asymmetric fibres to straight fibres with cylindrical asymmetry[25]. Thus, relatively straight Yankasa wool fibres should be expected to exhibit cylindrical asymmetry with a central core of orthocortex surrounded by an annular ring of paracortex.

The paracortex contains microfibril-matrix structure which is more regular than in the orthocortex. There is also a large amount of matrix relative to microfibrils in paracortex. Since the matrix stains more heavily with metals than the microfibrils, Crewther and others[5] have argued that the former is more heavily cross-linked with disulphide bonds. The fact that the paracortical cells have been found to possess greater cystine than the orthocortical cells have confirmed their claim.

The Medulla

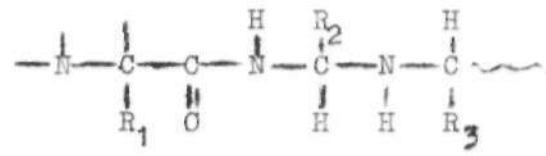
The medulla has an open structure with large number of vacuoles[26] in contrast to the compact, dense structure of the cuticle and cortex. This is because the protein synthesized during the growth in the follicle is in-adequate to fill the cell cavities and during desication of the cells, intracellular gaps appear and the final structure becomes open and light but stiff giving rise to a lighter, bulkier but stiff hair[26,27].

The medulla does not occur in fine wool fibressuch as the Australian Merino 64's but when present forms an axial stream of cells in the centre of the fibre. Yankasa wool appears to be coarse and Kazmi[28] claims that medulla exists within this fibre. The centre core ranges from a small amount of material which is not continous along the fibre to a large core in other cases accounting for more than 15% of the weight of the fibre[29]. It therefore appears to be largely amorphous in the electron microscope, although there is some evidence of fibrils[27]. The medulla contains proteins with a very low cystine content and large amount of citrulline[30,31].

CHAPTER 2

2.1 Amino acid Composition of wool

Wool protein consists of polypeptide chains of carbon and nitrogen, with hydrogen and oxygen atoms attached in the form of amino acid residues joined together as shown:-

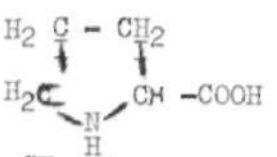
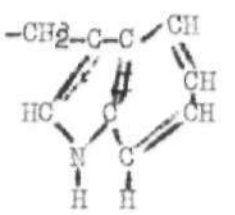


Amino acids are zwitterions, easily soluble in water but insoluble in organic solvents. Their composition is determined from the hydrolysate by means of column chromatography[32,33]. The amino acid content of merino wool given by Corfield and Robson[34], and Alexander and Hudson[35] are compared below in table I

Table 2.1.I

Amino acid content of Merino 64's wool

Amino Acid	Formula $NH_2-\underset{\displaystyle R}{\underset{\vert}{C}}H-COOH$	Nitrogen Content as % Merino 64 wool		
		Corfield et al.	Alexander and Hudson	
			Astbury	Harris
Alanine	$R = -CH_3$	4.12	4.13	4.40
Arginine	$-(CH_2)_3\ NH-C<^{NH}_{NH_2}$	19.1	10.30	10.40
Aspartic acid	$-CH_2COOH$	4.38	6.57	7.27
Cystine	$-CH_2.S.S.CH_2-$	7.30	11.90	12.20
Glutamic acid	$-(CH_2)_2COOH$	8.48	14.10	15.27
Glycine	$-H$	6.29	6.50	6.50
Histidine	$-CH_2-C=CH$ (N, NH, CH)	1.91	0.70	0.70
Isoleucine	$-CH.\ CH(CH_3)_2$	2.44	-	-
Leucine	"	5.85	11.30	11.30
Lysine	$-(CH_2)_4\ NH_2$	3.92	2.65	3.30
Methionine	$-(CH_2).S.CH_3$	0.32	0.70	0.71
Phenylalanine	$-CH_2.C_6H_5$	2.12	3.75	3.75

Proline		5.05	6.80	6.75
Serine	$-CH_2$ OH	8.66	10.30	9.41
Threonine	$-CH(OH) . CH_3$	5.12	6.40	6.76
Tryptophane		0.82	1.80	0.70
Tyrosine	$-CH_2 . C_6H_4$ OH	2.62	4.65	5.80
Valine	$-CH(CH_3)_2$	4.16	4.80	4.72
Amide nitrogen		6.73	1.13	1.40
Total		99.39	107.35	109.90

Kazmi[35] worked on the amino acid content of local merino and Yankasa wool and arrived at the following result shown in table 2.2.II

Table 2.1.II

Amino acid composition of wool

Amino Acid	Yankasa Wool		Merino Wool	
	μ mol / g	Res/1000	μ mol/g	Res/1000
Alanine	447	55	479	54
Arginine	597	74	625	71
Aspartic acid	545	67	566	64
Glutamic acid	1180	146	944	109
Cystine	725	89	989	111
Threonine	483	60	602	68
Serine	860	106	1014	115
Glycine	580	71	678	76
Proline	529	65	663	75
Methionine	41	5	30	3
Isoleucine	288	35	264	30
Leucine	655	81	640	72
Tyrosine	217	27	315	36
Phenylalanine	199	25	212	24
Lysine	291	36	253	28
Histidine	59	7	61	7
Valine	421	52	530	60

His results show that Yankasa wool has lower alanine, aspartic acid, cystine, threonine, serine, glycine, proline, tyrosine, phenylalanine, histidine and valine content but higher glutamic acid, methionine isoleucine, leucine, lysine content than local merino wool.

2.2 Reactivity of Wool Proteins

Keratin fibres, by their nature and origin are among the most heterogeneous materials to be subjected to physical and chemical studies. The reactivity of their proteins is attributed to the nature and structure of the groups present and can be altered by modifying the primary structure of the main polypeptide chain and the side chains of the component amino acids. Depressed or enhanced reactivity of a functional group in the protein can result from the influence of features characteristic of the protein environment or from interaction between the reagent and the protein environment, or from both. Thus, owing to the presence of a large number of various side chains, keratins are capable of taking part in a wide variety of chemical reactions resulting in the formation of disulphide cross-linkages between adjacent or parallel cystine chains; salt linkages between basic (lysine, and arginine) and acidic (glutamic and aspartic acids) group; and hydrogen bonds[1] between CO and NH groups in parallel folds or spirals, all acting along the fibre axis as shown in figure 2.2.2

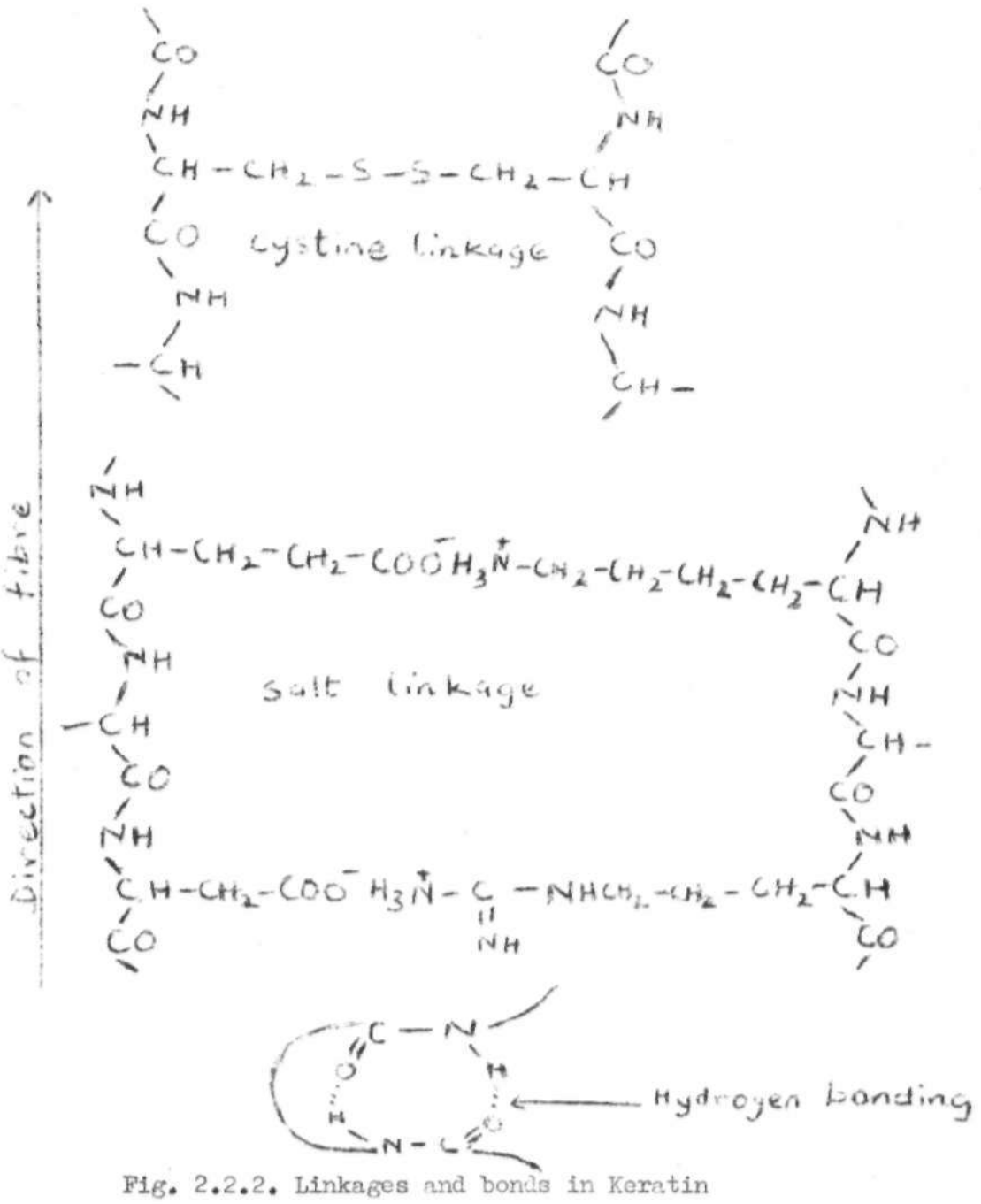


Fig. 2.2.2. Linkages and bonds in Keratin

These linkages through the side chains are responsible for the mechanical properties of the fibre. Middlebrook[37] established that the carboxyl groups in aspartic acid of wool are present as amides whereas **glutamic acid provides all the free carboxyl groups.**

The phenolic residue which is introduced into wool by the amino acid tyrosine is the centre of high reactivity and probably influences the chemical properties of the fibre significantly[35] as it is capable of forming powerful hydrogen bonding. Lundgren[38] suggested that two tyrosine residues may unite to form a phenolic ether cross-link between peptide chains. This reaction appears to explain the insolubility of the subcuticle membrane in solvents which can break hydrogen bonds after the oxidation of all the disulphide bonds.

The basic groups in wool are provided by the amino groups at the end of the peptide chains and side groups of lysine and arginine. Van Slyke[39] postulated the presence of a small proportion of hydroxylysine but concluded that it is unreactive when treated with dinitrofluoro-benzene. Middlebrook[40] later concluded that the side-chain amino group must be combined in wool in a way yet to be determined and suggested that these amino groups become free only on hydrolysis.

The relation between wool structure and reactivity was given by Dusenbury and Coe[41] who posulated that the orthocortex is more reactive than the paracortex since cystine which exercises some stabilizing effect is more in orthocortex. This view was upheld by Elliott and Roberts[42] who found reactive extensive network of intermacrofibrillar materials in the orthocortex.

CHAPTER 3

3.1 Interaction of Metal ions with Proteins

An insight into the possibility of metal ions to interact with proteins can be gained by utilising the following assumptions[43], which represent the general properties of proteins:-

a. The length of the peptide chain is much greater in proteins than in amino acids and small peptides. Therefore the side-chain groups such as carboxyl, imidazole or sulfhydryl are usually of much more importance in binding the metal ions than the terminal amino and carboxyl groups in amino acids.

b. There are usually several members of a given class of groups in a protein molecule. This means that the number of metal ions bound to a given class of groups depends both on the intrinsic affinity of ligand group for the metal ion and the number of such groups available to react.

c. The ligand groups in native protein are not free to move and cluster around a metal ion like small ligands. It follows that even when only a few metal ions are bound to a protein which carries many ligand groups, each metal ion may combine with only one ligand group. In such a case, the equilibrium at any one place of binding called a site, corresponds to the first successive series of equilibria seen with small ligands.

d. The protein molecule is a Zwitterion whose net potential field favours or hinders the approach of the metal ion. This means that the apparent affinity constants change as more and more ions are taken into account in interpreting the equilibria between metal ions and proteins.

e. A few ligands will be found in arrays which are sterically favourable for the chelation of particular metal ion in certain proteins. Such a cluster of groups may be present in the metal-free protein, and the affinity of this site for a given metal ion would be larger than the affinity of any component group of the cluster. On the other hand, the cluster may be formed by one particular configuration of the protein selected from a number of permissible configurations, or by a particular association of subunits of the protein. In other words, specific chelate effects are expected to be intimately related to protein structure and transformation of structure. The application of these assumptions will enable us to derive the fundamental equations that describe the interaction between metal ion and proteins.

3.2. Theory of metal ion binding to single ligand groups

The association between any molecule or ion and a site i on a protein molecule was described by Gurd et al.[43] with the equation

$$\frac{(iJ)}{(i0)} = K_{iJ} \frac{\gamma_{i0}}{\gamma_{iJ}} a_J = K_{iJ} \bar{\iota}_J a_J \quad \ldots$$

where (iJ) is the probability that J is associated at site i and (i0) is the probability that no molecule or ion is associated at site i.

KiJ is the intrinsic association constant for the reaction, γ_{iJ} and γ_{i0} are the activity coefficients of the protein molecules with and without J at site i, respectively, and aJ is the activity of J. τ_J is the ratio γ_{i0}/γ_{iJ}, i is omitted, since the value of τ_J is taken to be the same no matter which site binds J. This is consequence of the assumption that the reaction at one site is uninfluenced by reaction at another except insofar as the alteration in the net charge borne by the protein molecule causes a corresponding change in the electrical work invôlved in the approach of an ion to a binding site. The value of τ_J is therefore a function of the composition of the solvent and the charge on the protein molecule, but is independent of the nature of the site. On the other hand, KiJ depends only on the nature of the site and emerges as a true thermodynamic constant if aJ is referred to a standard state of infinite dilution and τ_J is referred to dilute protein of zero net charge.

When the association of a metal ion M is considered, equation (1) becomes

$$\frac{(iM)}{(i0)} = KiM \frac{\gamma_{i0}}{\gamma_{iM}} aM = KiM \tau_M aM \quad \text{---- (2)}$$

where iM, KiM, iM, aM and τ_M have meanings corresponding to those assigned for J. Since the sum of all probabilities that a single site i is either open or associated with a molecule or ion J is equal to unity, then

$$i0 + \sum_J (iJ) = 1 \quad \text{-------(3)}$$

Applying Scatchards principle[44], it is possible to consider the whole protein molecule with several different classes of sites i, and each ni in number. The average number of molecules or ions of any type J bound to any class of site i is designated by $\bar{\nu}_{iJ}$ which is equal to ni(iJ). Consequently, $\bar{\nu}_{iM}$ equals ni(iM).

By summing the values of $\bar{\nu}_{iM}$ over all classes of sites, we obtain the quantity

$$\bar{\nu}_{M} = \sum_{i} \bar{\nu}_{iM}$$

which is the average number of metal ions bound to all possible sites of one molecule. By combining equations (1), (2) and (3) the general equation of binding is obtained as

$$\bar{\nu}_{iM} = \frac{niKiM\, \tau_M\, aM}{1 + \sum_{J} KiJ\, \tau_J\, aJ} \qquad \text{——(4)}$$

or

$$\bar{\nu}_{M} = \sum_{i} \bar{\nu}_{iM} = \sum_{i} \frac{niKiM\, \tau_M\, aM}{1 + \sum_{J} KiJ\, \tau_J\, aJ} \qquad \text{——(5)}$$

3.3. Competition between Metal ions and Hydrogen ions

Most of the chemical groups in a protein molecule that may be expected to combine with metal ions are also capable of combining with hydrogen ions, and in general there will be competition for sites in the protein. The equilibria existing between metal ions and protein ligands apply similarly to hydrogen ions. Figure 3.3. III represents a hypothetical i^{th} class of ni identical groups (carboxyl, imidazole or E-amino etc.), $\bar{\nu}_{iH}$ of which are combined with hydrogen ions and $\bar{\nu}_{iM}$ of which are combined with some other cations, M.

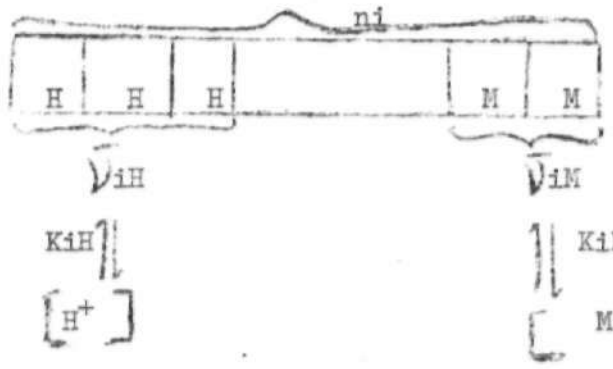


Fig. 3.3.3: Equilibria of hydrogen and metal ions with ni identical sites of i^{th} class in a protein. $\bar{\nu}$iH and $\bar{\nu}$iM represent the average number of hydrogen and metal ions bound to this class of sites.

There remains (ni- $\bar{\nu}$iH - $\bar{\nu}$iM) groups in the uncombined (or conjugated base) form. It can be deduced from equation (1) that

$$\frac{\bar{\nu}iM}{\bar{\nu}iH} \doteq \frac{ni(iM)}{ni(iH)} = \frac{KiM\ \bar{\tau}M\ aM}{KiH\ \bar{\tau}H\ aH}$$

$$\text{or} \qquad KiM = \frac{\bar{\nu}iM\ KiH\ \bar{\tau}H\ aH}{\bar{\nu}iH\ \bar{\tau}M\ aM} \qquad \text{----(6)}$$

Equations (4) and (6) when combined give two equations which describe the equilibria for each ion:

$$\bar{\nu}iH = KiH\ \bar{\tau}H\ aH\ (ni - \bar{\nu}iH - \bar{\nu}iM) \qquad \text{----(7)}$$

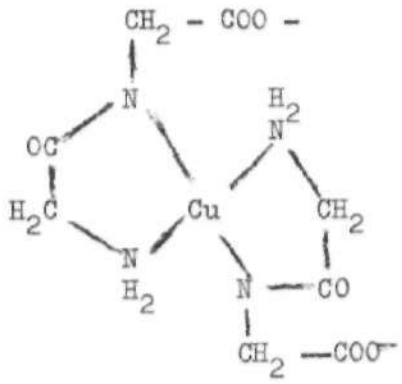
$$\bar{\nu}iM = KiM\ \bar{\tau}M\ aM\ (ni - \bar{\nu}iH - \bar{\nu}iM) \qquad \text{----(8)}$$

Hydrogen ion competition can be most readily detected by observing a shift in pH following the addition of a metal salt to an unbuffered protein solution. When the added ions enter into competition with hydrogen ions for sites, a rise in aH (fall in pH) should occur according to equation (7) provided that the test is restricted to the pH range where hydrolysis of the metal ion can be neglected.

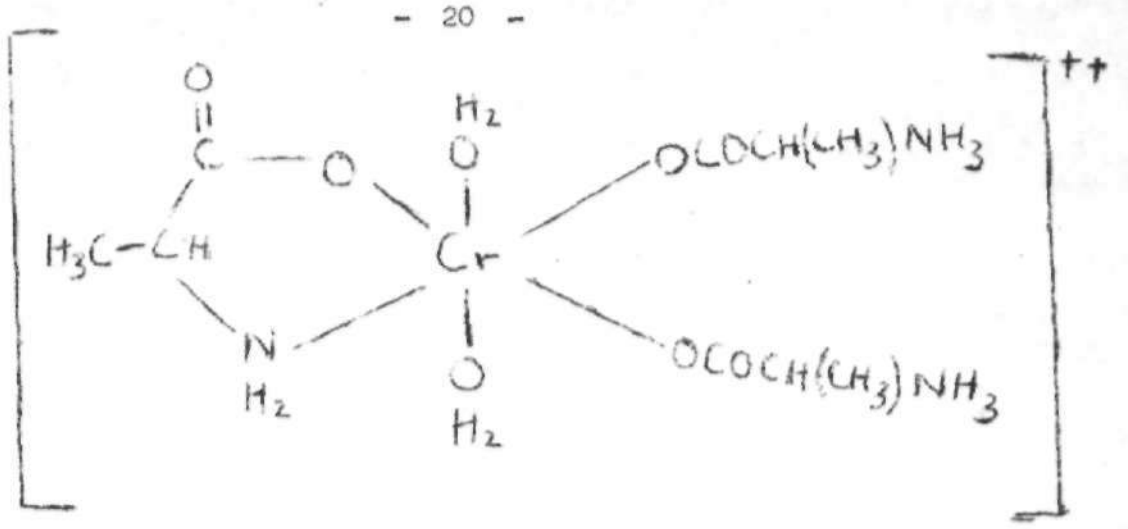
3.4. Metal ion binding to Proteins

Proteins, with their many reactive side chains have the potential capacity to bind most metals very tightly. During such binding, the metal ions serve as cross link between peptide chains resulting in metal-protein complexes. In such complexes, the metal ions act as recipients of electron pairs from donor atoms in the protein ligand groups[45,46] resulting in the formation of Sp^3, dsp^2, and d^2sp^3 hybridisation. Each of the natural amino acids in a protein is capable of forming a stable, five-membered chelate ring with a metal atom. In the common skeleton, $NH_2 - CHR - COO^-$, two effective donor atoms are separated by three bonds. Some of the amino acids have effective donor atoms in the side chain, R, and these may enter into complex formation and may compete with the α-amino and carboxyl groups. Mattock[47] has pointed out that the metals which tend to form polynuclear complexes are those which form metal-oxygen bonds with comparable amounts of ionic and covalent character. Sen et al[48] showed with IR absorption that N - metal bonds in crystalline Cu^{II} are largely covalent whereas the O - metal bonds are essentially ionic. Greenwald[49] presented evidence for the complexes of glycine with alkaline

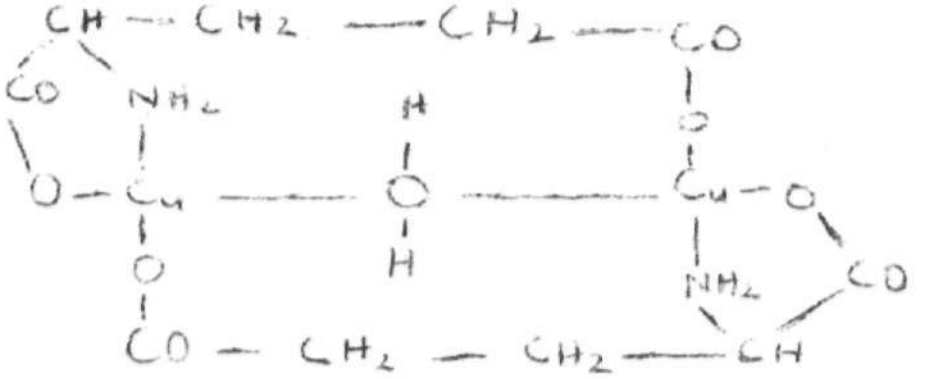
earth ions and proposed that the metal-carboxylate bonds have the form $MOOCCH_2NH_3^{++}$. This agrees with the complexes of Cu^{II} with dipolar forms of glycine and alanine put forward by Borsook and Thimann[50]. The studies of the complexes of Cu^{II} by Pedersen[51] yielded evidence for the formation of dimers which he formulated as $\left[(H_2O)_7\ Cu_2OH\right]^{+++}$ and $\left[(H_2O)_6\ Cu_2(OH)_2\right]^{++}$ while Dobbie and Kermack[52] showed that a reaction between $CuCl_2$ and dipolar glycylglycine in molar ratio of 1:2 led to a coordination between Cu^{II} and the peptide nitrogen resulting in the ionization of two protons thus:



Amino acid ligands may combine with metal ion in more than one way in the same complex. This is common to trivalent metals, Al, Cr, Ce which bond tightly to oxygen in preference to nitrogen and show a strong tendency to form polynuclear complexes at lower pH values[53]. This view was shared by Green and Ang[54] whose studies showed that certain Cr^{III} complexes of alanine may contain alanine partially in chelate combination and partially in coordination through carboxylate groups alone as shown:



Sarma[55] identified two different, well-defined complexes from a reaction between Cu^{II} and glutamate in the ratios of 1:2 and 2:2. He was of the view that the former resembled glycine complex and was obtained when Cu^{II} was chelated through α-amino and carboxyl groups. The latter complex, which was slightly soluble and held one molecule of water in the crystal very tightly, appear to have a structure shown below:



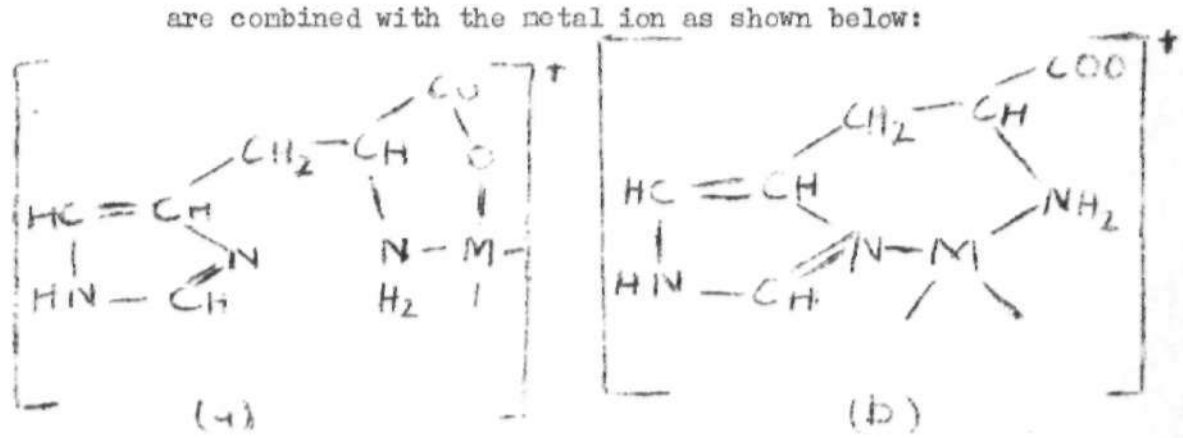
Histidine and cystine combine most strongly with metal ions to form complexes[47,56]. Combination involving histidine may be either through:-

a. the usual five-membered ring with carboxylate and α- amino groups;

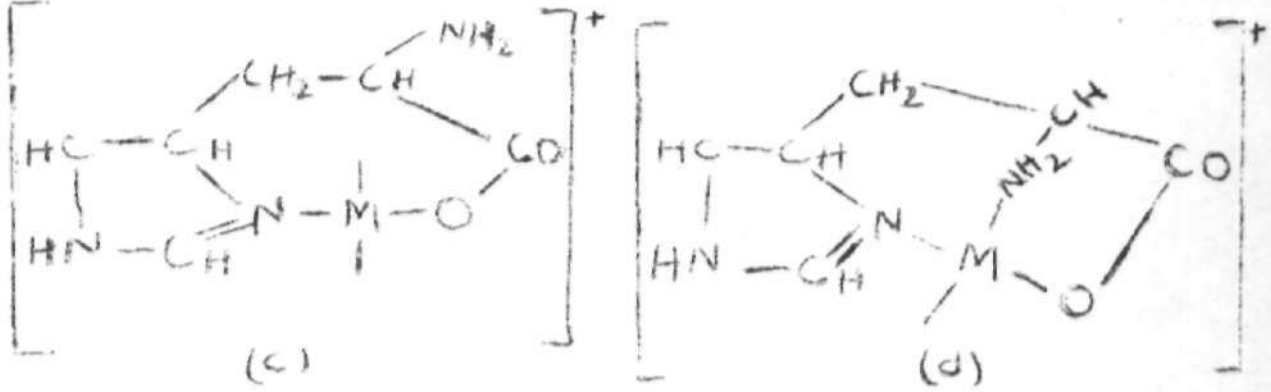
b. six-membered ring involving the α-amino and imidazole groups;

c. a seven-membered ring involving the carboxylate and imidazole groups;

d. a structure in which all three donor groups of histidine are combined with the metal ion as shown below:



(a) (b)



(c) (d)

None of these structures may be ruled out under all circumstances. Structure (c) is probably negligible except perhaps under relatively acid conditions where the α-amino group is not free to react, otherwise the larger ring should be at a considerable disadvantage. Structure (b) may be favoured by those metal ions that show a

preference for nitrogen atoms[57]. Spectral evidence by Edsall et al.[58] showed that in Cu^{II} - dihistidinate complex, the cupric ion is bonded to two imidazole groups and two α-amino groups. The studies of Maley and Mellor[59] as well as those of Irving et al.[60] on Cu^{II} - histidine reactions are in support of structure (b) as the plausible interpretation of Cu^{II} - histidine interaction.

Cysteine combines with many metal ions more strongly than any other amino acid. It is readily oxidized by Cu^{II} in excess ammoniacal solution to cystine[61] according to the equation

$$4RS^{-} + 2Cu^{2+} = 2RSCu + RSSR.$$

The remaining sulphur containing amino acid, methionine, appears to combine with Cu^{II} to an extent of monoaminocarboxylic acids[62], and there is little doubt that the carboxyl and amino groups are responsible for chelation with metal ions.

CHAPTER 4

4.0 MATERIALS, METHODS AND RESULTS

4.1 Preparation of Wool Samples

Yankasa wool fibres were taken in thimbles and inserted into a soxhlet extractor fitted with a condenser. The fibres were refluxed with diethyl ether at 40°C for 4 hrs to remove the normal contaminants of keratin fibres. The fibres were further purified by refluxing with absolute ethanol for 6 hrs. They were then washed clean in several changes of distilled water to remove alcohol and attain their isoionic point. The fibres were allowed to dry in laboratory air current and conditioned in a desiccator over saturated ammonium nitrate solution at relative humidity (RH) of between 50 - 65% and 22°C for seven days. These fibres so treated are referred to as conditioned native Yankasa wool in subsequent tests.

4.2 Chemical modification of wool

This was an attempt to produce a net positive charge on Yankasa wool and thus depress its reactivity with metal ions as discussed earlier on in section 2.2. Two methods were used - esterification and acetylation.

4.2.1. Esterification of Wool

The esterification of protein carboxylic groups[63,64] involves nucleophilic attack by RO^- on the carbonyl carbon of the carboxylic acid residue followed by the displacement of -OH by -OR.

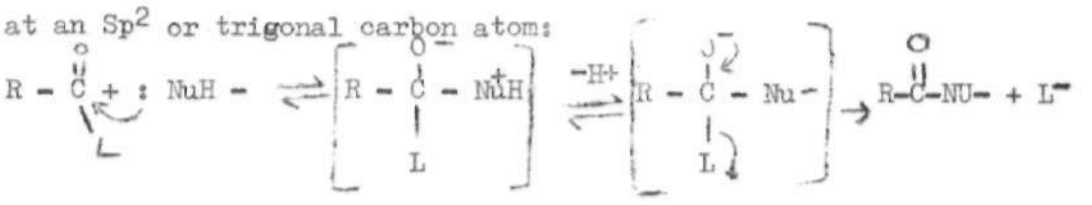
$$CH(CH_2)_{1,2}- COOH + RO^- \longrightarrow CH(CH_2)_{1,2}— COOR + OH-$$

Current reagents used in blocking the carboxyl groups of proteins merely yield partial result. The esterification of wool with alcohols containing a catalytic amount of hydrochloric acid was originally thought to be specific for carboxyl groups.[65,66] Evidence so far adduced show that this reaction causes some modification of amide and other groups [67,68,69]. However, despite a modification of the technique by Bello,[70] alcohol and hydrochloric acid catalyst have remained the most suitable and dependable method of esterifying wool.[69]

Conditioned Yankasa wool dried to constant weight at 105°C was treated with absolute ethanol in the ratio 50:1 (V/W) in a round bottom flask fitted with reflux condenser after the method of Fraenkel - conrat and Olcott.[71] Sufficient 0.1 N. hydrochloric acid was added and refluxing was allowed to take place at 60°C for 6 hours. Esterified wool was washed thoroughly in several changes of distilled water and dried in laboratory air current. The wool fibres were then reconditioned in a desiccator over saturated ammonium nitrate solution at RH of 50 - 65°C and 22°C for seven days.

4.2.2. Acetylation of Wool

The reagents employed in the acetylation of proteins have a common mechanistic feature which involves at attack of a nucleophile (NuH-) at an Sp^2 or trigonal carbon atom:



Blackburn and Phillips[72,73] reported that acetic acid alone was capable of acetylating some of the amino groups in wool.

Elliott and Speakman[74] blocked a large amount of amino groups in wool with a mixture of acetic anhydride and glacial acetic acid in the presence of sulphuric acid. Alexander et al[75] obtained 90% acetylation of wool by adding dimethylaniline to wool sample in acetic anhydride, glacial acetic acid and small amounts of sulphuric acid under carefull controlled conditions.

Conditioned Yankasa wool fibres dried to constant weight at 105°C were treated with a 1:1 mixture of acetic anhydride and glacial acetic acid in a flask fitted with a reflux condenser after the method of Needles.[64,76] The fibres were refluxed at 50°C for 20 hours. The resulting acetylated wool fibres were washed in aqueous sodium acetate followed by further washing in several changes of distilled water and dried in air. The dry wool fibres were reconditioned in a desiccator containing saturated ammonium nitrate solution at RH 50 -65 and 22°C for seven days.

4.3 Moisture regain of Yankasa Wool

Moisture regain in wool is the weight of water which a perfectly dry sample would have to regain on exposure to the griginal atmospheric conditions. Measurements involving hygroscopic materials like wool are influenced to some extent by changes in the relative humidity of the atmosphere. Hoare and Thompson[77] established an average difference of about 0.2% or less when the relative humidity changed by 10%.
Moisture regain (R) for wool is calculated from the expression,

$$R = \frac{m_1 - m_2}{m_2} \times 100$$

where m_1 is the weight of conditioned wool, and m_2 is the weight of completely dry wool. Duplicate samples of conditioned, modified and metal ion treated Yankasa wool fibres were weighed, and dried in an oven at 105°C for 6 hours. The samples were then heated to constant weight for another 2 hours in the oven. The average regain was calculated in each case on the basis if above formular as shown in Table 4.3.III

4.4 Absorption of Metal ions by Wool

4.4.1 Absorption of Copper ions by Wool

One gram of duplicate samples of conditioned native and modified Yankasa wool fibres corrected for regain was treated with 100 cm^3 of 0.1M aqueous solution of copper II chloride (PH 4.18) at 25°C for 24 hours. After treatment, the solution was decanted and the wool was washed thoroughly and carefully with changes of distilled water. The decanted solution and washings were made up to 250cm^3 in a volumetric flask and the concentration of unabsorbed copper ion was determined volumetrically using the redox method suggested by Vogel[78]. The copper ion content of equivalent volume of original copper II chloride solution was also determined and the weight of copper ion absorbed by one gram of wool was found in each case by difference as given in Table 4.4.IV

(a) Copper II ion absorbed native and modified Yankasa wool fibres obtained from section 4.4. 1 were digested with 10 cm^3 of concentrated nitric acid and heated strongly to expel nitrogen dioxide. The resulting solution in each case was made up to

100 cm^3 in a volumetric flask and then filtered. The filtrate was fed into Unicam SP 1900 atomic absorption spectrophotometer and from the absorbance obtained, the concentration of the sample was read from a standard calibration curve and hence the weight of copper II ion absorbed by each wool was calculated and given in table 4.4.IV

4.4.2. Absorption of Chromium ion by Wool

One gram of duplicate samples of conditioned native and modified Yankasa wool fibres corrected for moisture regain was soaked in 100 cm^3 of 0.1M aqueous solution of chromium nitrate PH 2.95-3 at 25 °C for 24 hours. After absorption, the solution was decanted and the woool was carefully washed with distilled water. The washings and decanted solution were made up to 250 cm^3 in a volumetric flask and the concentration of unabsorbed chromium ion was determined volumetrically using oxidation method involving ammonium persulphate and silver nitrate catalyst as proposed by Vogel[78]. The weight of chromium ion in fresh chromium nitrate of equal volume was also determined and the weight of chromium ion absorbed by wool in each case was obtained by difference and given in table 4.4.IV

4.4.3 Absorption of Cerous ion by Wool

One gram of duplicate samples of conditioned native and modified Yankasa wool fibres corrected for moisture regain was soaked in 100 cm^3 of 0.01M solution of cerous sulphate in sulphuric acid at 25 °C for 24 hours. The concentration of unabsorbed cerous ion was determined from 250 cm^3 of the decanted solution and washings using oxidation reaction involving ammonium persulphate, 0.1N silver nitrate, ferrous

ammonium sulphate and N-phenylanthranilic acid indicator as proposed by Vogel[78]. The concentration of cerous ion in equivalent volume of original cerous sulphate solution was then determined and the weight of cerous ion absorbed by wool in each case was obtained by difference as shown in table 4.4.IV

4.4.4 Absorption of Aluminium ion by Wool

One gram of duplicate samples of conditioned native and modified Yankasa wool fibres corrected for moisture regain was soaked in 100 cm^3 of 0.01M aqueous solution of aluminium sulphate at P^H 4.12 and 25 ^oC for 24 hours. The weight of unabsorbed aluminium ion in the decanted solution and washings was determined by complexometric titration involving 0.01M EDTA, 0.01M-Zinc sulphate and Eriochrome Black T indicator as suggested by Vogel[78]. The weight of Aluminium ion in equivalent volume of original aluminium sulphate solution was also determined and the weight of aluminium ion absorbed by each wool was obtained by difference as shown in table 4.4.IV

4.5 Effect of Metal ion absorption on some mechanical properties of Wool.

Native and modified Yankasa wool fibres were soaked in solutions of aluminium sulphate, chromium nitrate, copper II chloride and cerous sulphate respectively for 24 hours at room temperature. The wool samples were thoroughly washed with distilled water, dried in air and reconditioned at R.H of 50-65% and 22^{o}C for two days. The fibres were individually subjected to constant rate of elongation in an instron

tester using a guage length of 5 cm, magnification ratio of 1:5 and a load cell of 500g range with 200g full-scale load calibration. The average stress against strain for seven fibres of each group was poltted and shown in figures 4.5.4 - 8. The tensile test results are shown in table 4.5.VI

4.6 Competition between metal ions and hydrogen ions.

Equal weights (0.1g) of conditioned native Yankasa wool fibres corrected for regain were soaked in 50 cm^3 of aluminium sulphate, copper II chloride, chromium nitrate and cerous sulphate solutions each containing 100,200,300,400,500,1000 ppm of the metal ions respectively. The competition between the metal ions and hydrogen was followed with the aid of a P^H meter model 290 MK 2 Pye Unicam for 24 hours. The change in P^H is shown in table 4.6.VII, VIII and IX

4.7 Infrared absorption of Yankasa Wool

This technique provides a powerful method of determining the structure of solid materials like wool. It is based on the assumption that each distinct type of molecule has a characteristic vibration spectrum from where the structure can be deduced.

2 mg of dry native, modified and metal ion absorbed Yankasa wool fibre chips were each thoroughly ground to powder with 100mg of potassium bromide (AR) and compressed into a thin disc. The spectrum of each wool sample fig. 4.7.9-15 is recorded against KBr standard with the aid of Perkin Elmer Model-700 Infrared spectrophotometer. The absorption intensities obtained from the Spectra are given in tables X and XI.

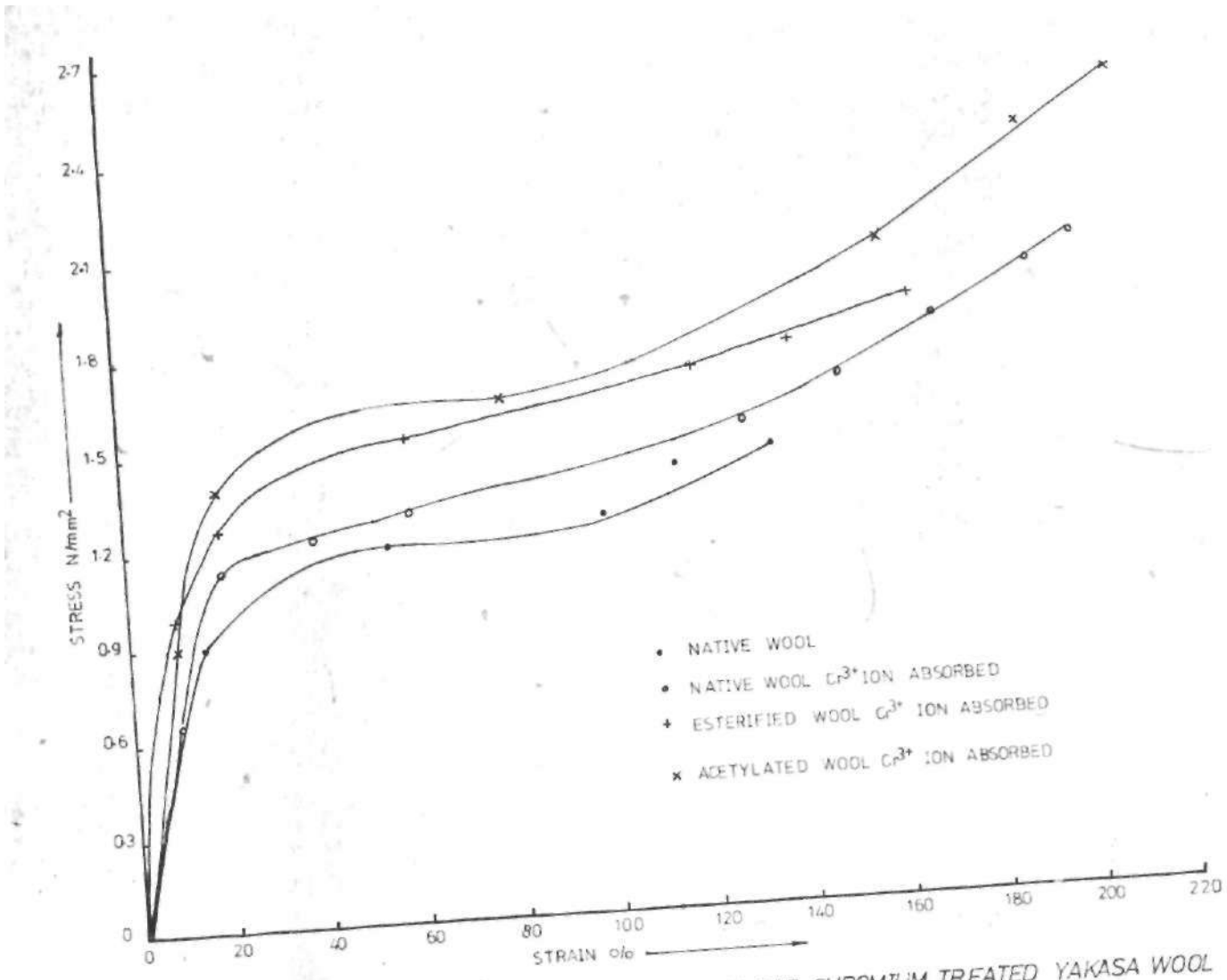


Fig. 4.5.4 STRESS-STRAIN CURVE FOR CHROMIUM TREATED YAKASA WOOL

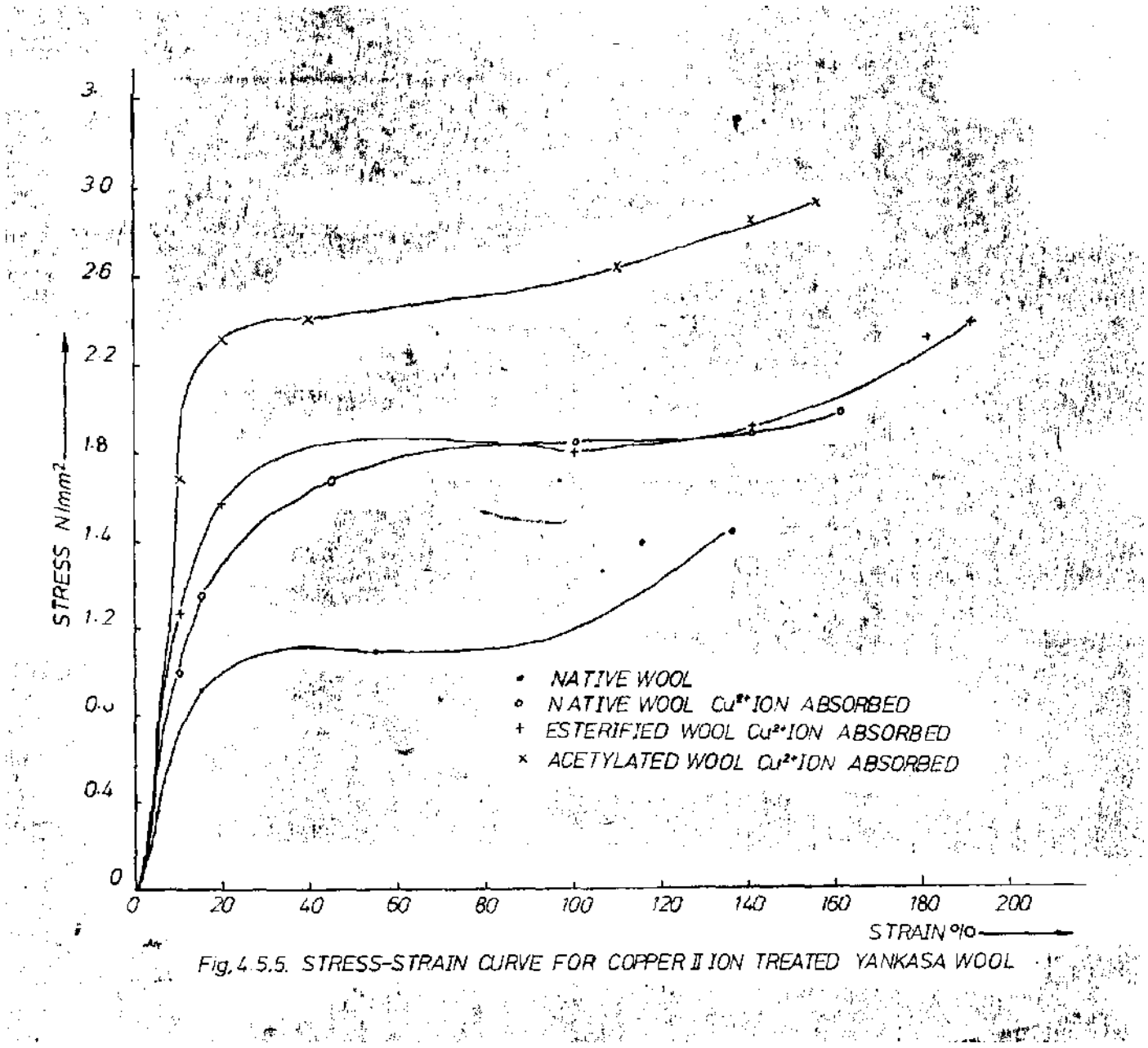


Fig. 4.5.5. STRESS-STRAIN CURVE FOR COPPER II ION TREATED YANKASA WOOL

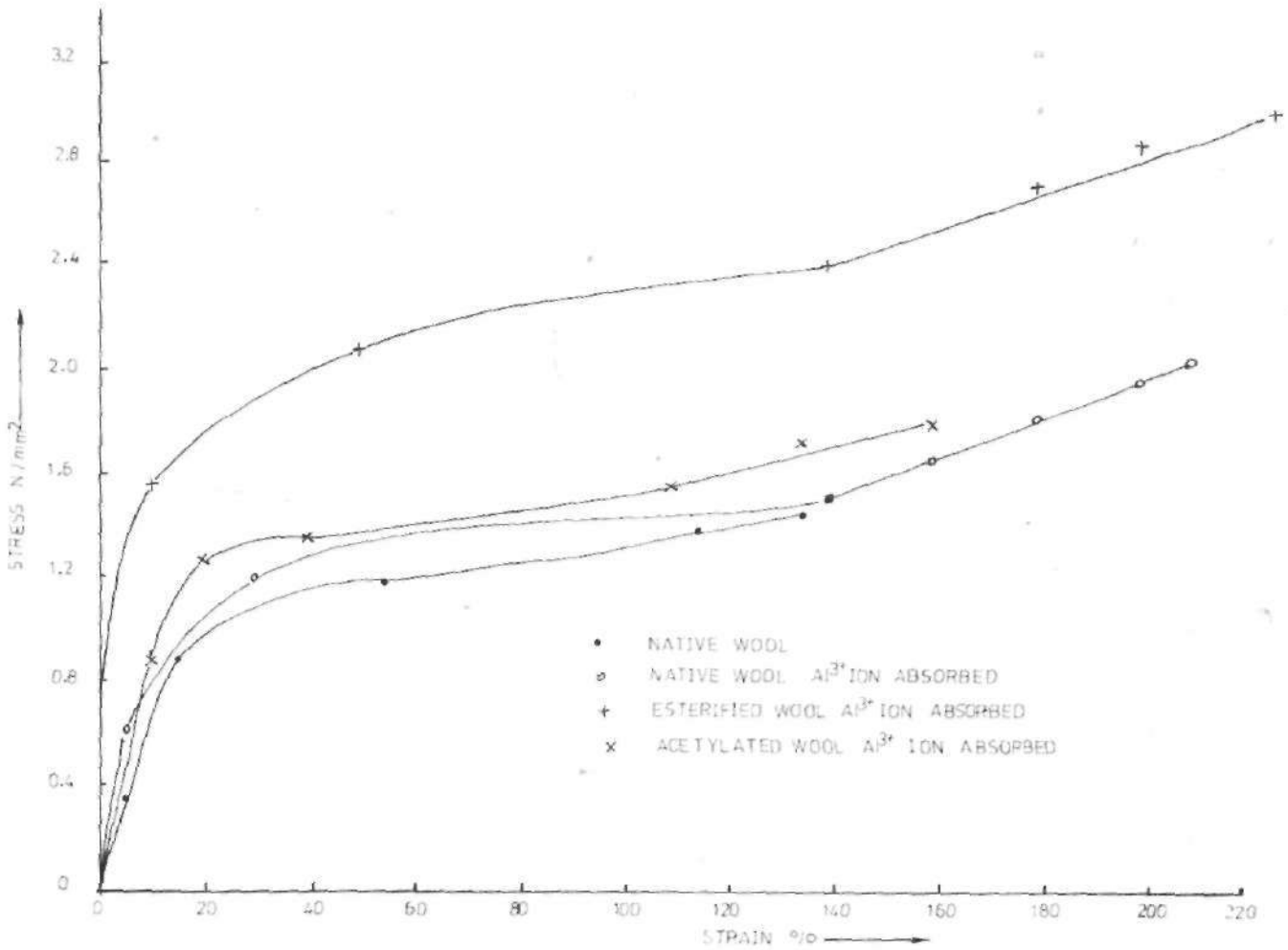


Fig. 4.5.6. STRESS–STRAIN CURVE FOR ALUMINIUM ION ABSORBED YANKASA WOOL

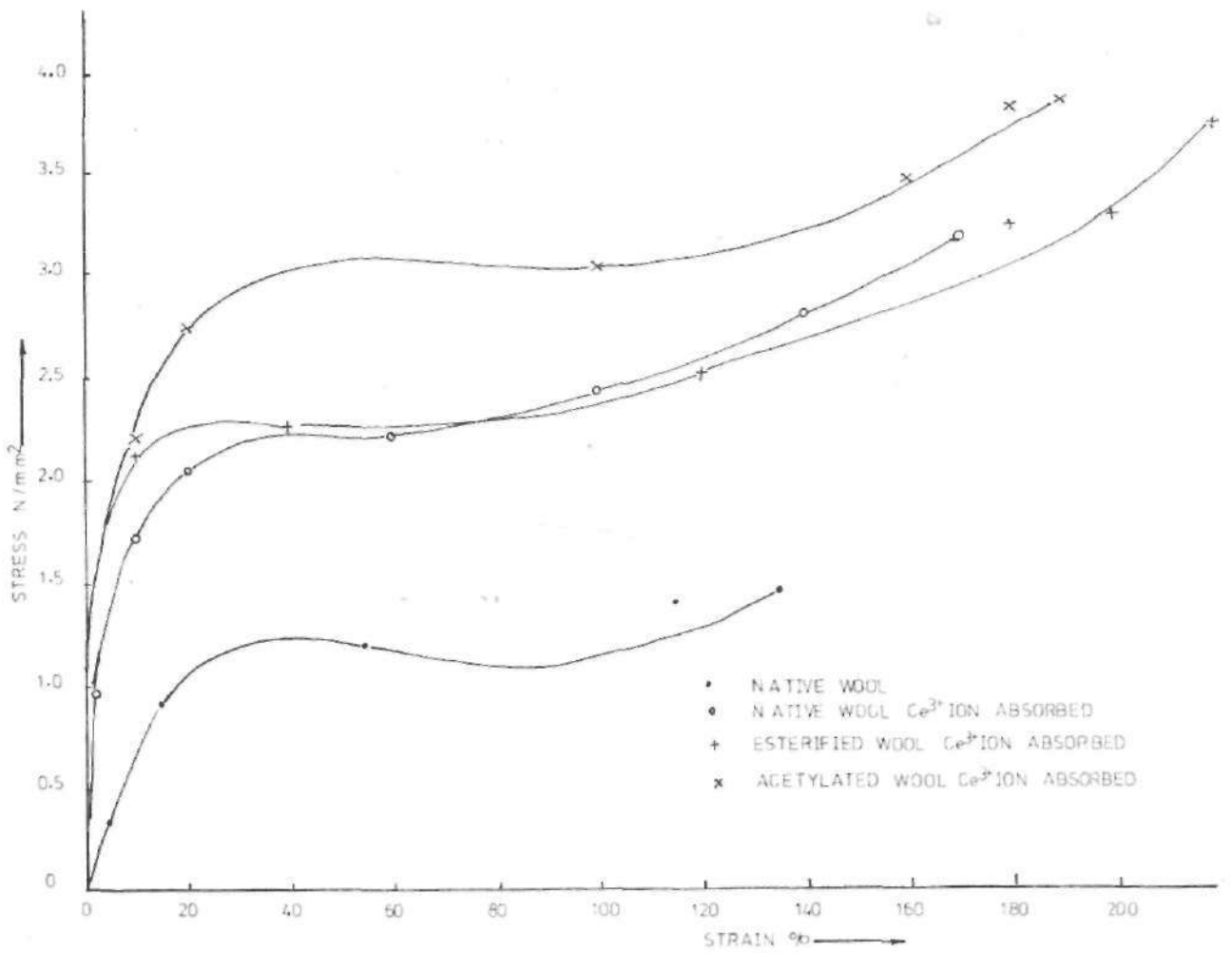


Fig.4.5.7. STRESS–STRAIN CURVE FOR CEROUS ION ABSORBED YANKASA WOOL

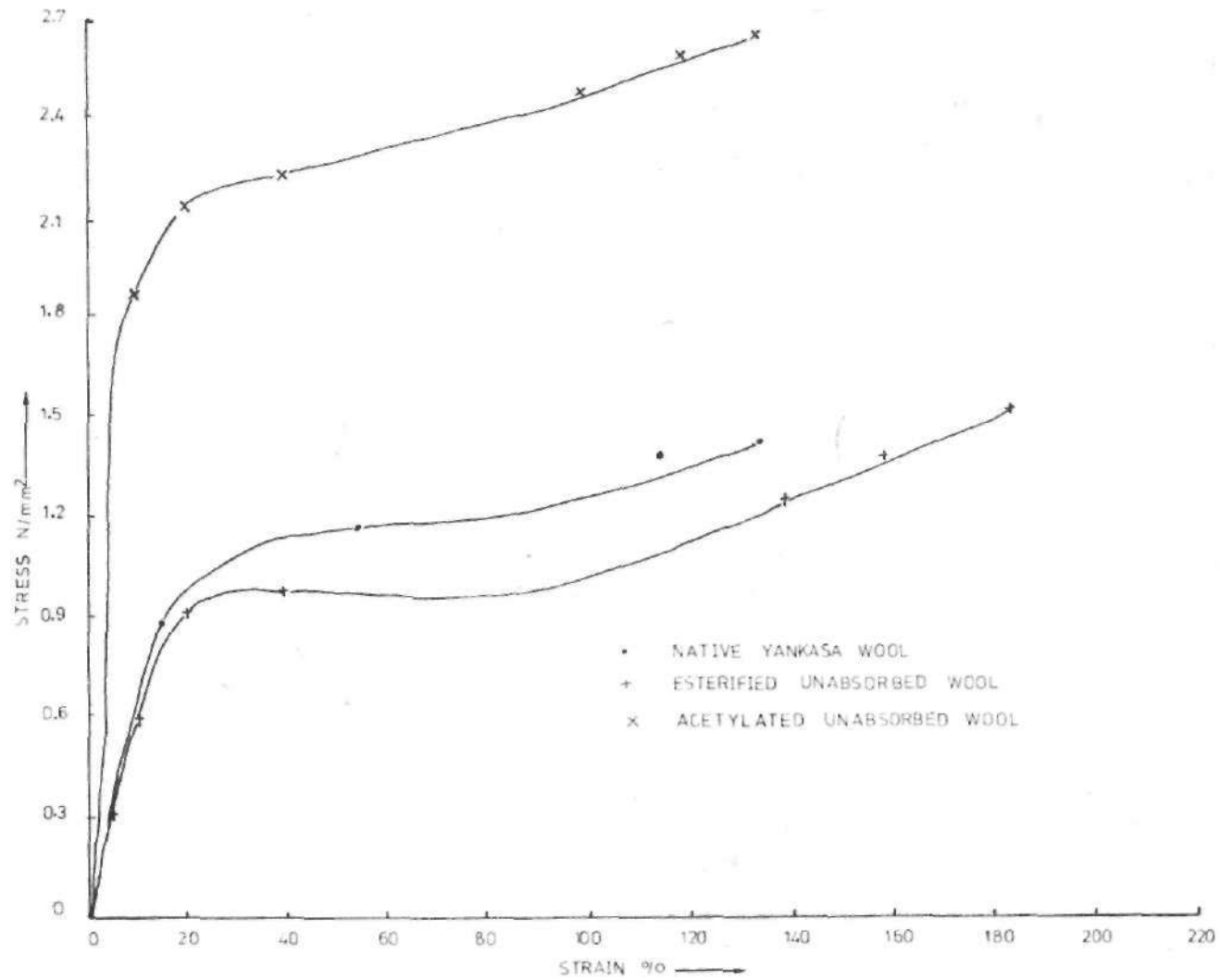


Fig. 4.5.8. STRESS–STRAIN CURVE FOR NATIVE AND MODIFIED YANKASA WOOL

Table 4.3.III. Moisture regain of Wool

Treatment	Regain %
Native Yankasa Wool	11.9
Esterified Yankasa Wool	9.7
Acetylated Yankasa Wool	9.2
Native Yankasa + Copper Chloride	8.3
Native Yankasa + Cerous Sulphate	10.9
Native Yankasa + Chromium nitrate	9.2
Native Yankasa + Aluminium sulphate	9.5

Table 4.4.IV. Metal ion absorbed by native and Modified Wool

Treatment	Conc.(g) metal ion/g wool $x10^{-2}$	Calculated m. equiv. metal/g. Wool	Colour of treated Wool
Native Wool + Al^{3+}ion	0.11	0.04	White
Native wool + Cr^{3+}ion	2.27	0.44	Light blue
Native wool + Cu^{2+}ion	2.20	0.35	Green
Native wool + Ce^{3+}ion	1.24	0.09	White
Esterified wool + Al^{3+}ion	0.08	0.03	White
Esterified wool + Cr^{3+}ion	1.95	0.38	Light blue
Esterified wool + Cu^{2+}ion	1.55	0.24	Light green
Esterified wool + Ce^{3+}ion	0.41	0.03	White
Acetylated wool + Al^{3+}ion	0.03	0.01	Brown
Acetylated wool + Cr^{3+}ion	1.40	0.27	Brown
Acetylated wool + Cu^{2+}ion	0.90	0.14	Brown with green tinge
Acetylated wool + Ce^{3+}ion	0.07	0.005	Brown

Table 4.4.V: Copper ion absorbed by wool

Treatment	Concentration (g) metal ion absorbed/g wool $X10^{-2}$	Calculated m.equi-vmetal/g wool
Native Yankasa + Cu^{2+}ion	3.40	0.54
Esterified Yankasa + Cu^{2+}ion	2.00	0.31
Acetylated Yankasa + Cu^{2+}ion	0.40	0.06

Table 4.5.VI. Effect of metal ion uptake on the mechanical Properties of native and modified Yankasa wool.

Treatment	Ultimate Tensile strength (UTS) Nmm^2	Ductility or Breaking Extension %	Toughness or Work of Rupture Nmm^2/Ext. %	Resilience or Modulus Nmm^2/Ext.%	Yield Stress Nmm^2	Yield Strain %
Native Wool	1.45	135	15.03	0.36	1.05	26
Unabsorbed Esterified Wool	1.54	185	19.95	0.39	0.97	13
Unabsorbed Acetylated Wool	2.65	135	31.33	-	2.15	19
Native Wool + Cu^{2+} ion	2.10	160	30.05	0.29	1.50	30
Native Wool + Cr^{3+} ion	2.05	200	28.83	0.37	1.16	23
Native Wool + Ce^{3+} ion	3.18	178	42.00	0.14	2.07	21.5
Native Wool + Al^{3+} ion	2.03	210	30.84	0.06	1.22	23
Esterified Wool + Cu^{2+} ion	2.41	190	39.24	0.64	1.68	25
Esterified Wool + Cr^{3+} ion	1.89	165	25.61	0.50	1.35	25
Esterified Wool + Ce^{3+} ion	3.74	220	57.67	-	2.15	12
Esterified Wool + Al^{3+} ion	3.10	225	54.36	-	1.30	22
Acetylated Wool + Cu^{2+} ion	2.94	155	41.57	0.47	2.26	17
Acetylated Wool + Cr^{3+} ion	2.55	210	37.92	0.06	1.44	22.5
Acetylated Wool + Ce^{3+} ion	3.85	190	59.43	-	2.80	22.5
Acetylated Wool + Al^{3+} ion	1.80	160	23.63	0.55	1.26	22

Table 4.6.VII: Competition between Aluminium and hydrogen ions.

Time (hrs)	Concentration (ppm)	100	200	300	400	500	1000
		PH	OF	BATH			
0		4.30	4.17	4.13	4.08	4.04	3.91
1		4.34	4.20	4.17	4.09	4.05	3.93
2		4.38	4.22	4.15	4.09	4.05	3.91
3		4.41	4.28	4.17	4.13	4.07	3.96
4		4.48	4.40	4.32	4.24	4.23	4.09
5		4.56	4.43	4.35	4.28	4.24	4.12
23		4.63	4.50	4.46	4.40	4.30	4.22
24		4.65	4.49	4.42	4.37	4.33	4.21
25		4.58	4.45	4.42	4.35	4.33	4.18

Table 4.6.VIII: Competition between Cupric and hydrogen ions.

Time (hrs)	Concentration ppm.	100	200	300	400	500	1000
		PH	OF	BATH			
0		6.02	5.81	5.60	5.50	5.54	5.20
1		6.03	5.76	5.64	5.52	5.58	5.32
2		5.99	5.81	5.63	5.56	5.58	5.33
3		5.78	5.61	5.50	5.42	5.46	5.31
4		5.49	5.31	5.25	5.19	5.30	5.15
5		5.43	5.30	5.23	5.25	5.32	5.18
27		5.48	5.23	-	-	-	-

Table 4.6.1X: Competition between Chromium and hydreogen ions.

Concentration (ppm)	100	200	300	400	500	1000
Time (hrs)	PH	OF	BATH			
0	4.00	3.90	3.85	3.77	3.76	3.55
1	4.10	3.96	3.88	3.82	3.74	3.63
5	4.19	4.01	3.91	3.86	3.83	3.65
6	4.20	4.01	3.92	3.87	3.87	3.69
7	4.23	4.01	3.93	3.90	3.86	3.71
8	4.26	4.07	3.98	3.91	3.87	3.69
22	4.22	4.02	3.95	3.87	3.84	3.66
24	4.20	4.00	3.87	3.83	3.79	3.64
25	4.21	4.01	3.90	3.82	3.80	3.61

Table 4.7.X: Infrared absorption of native and modified Yankasa Wool

Native Yankasa Wool		Esterified Yankasa		Acetylated Yankasa Wool	
Frequency cm^{-1}	Absorption	Frequency cm^{-1}	Absorption	Frequency cm^{-1}	Absorption
3300	0.646	3300	0.372	3250	0.256
2950	0.529	2940	0.310	2950	0.222
1700	0.658	1700	0.367	1700	0.240
1670	0.733	1668	0.398	1668	0.256
1578	0.602	1575	0.328	-	-
1560	0.658	1558	0.362	1558	0.237
1540	0.686	1540	0.377	1540	0.252
1460	0.575	1450	0.337	1440	0.229

Table 4.7.XI: Infrared absorption of metal ion treated Yankasa Wool

Native Wool + Al^{3+}		Native Wool + Cr^{3+}		Native Wool + Cu^{2+}		Nativem Wool + Ce^{3+}	
Frequency cm^{-1}	Absorption	Frequency cm^{-1}	Absorption	Frequency cm^{-1}	Absorption	Frequency cm^{-1}	Absorption
3270	0.699	3250	0.658	3250	0.810	3300	0.620
-	-	2960	0.523	2880	0.678	2980	0.569
1708	0.658	1700	0.678	1700	0.731	1700	0.620
1674	0.733	1670	0.770	1668	0.783	1670	0.646
1560	0.678	1560	0.686	1560	0.752	1560	0.627
1540	0.699	1540	0.710	1540	0.770	1640	0.646
1460	0.627	1455	0.620	1455	0.745	1450	0.699

CHAPTER 5

DISCUSSION AND CONCLUSION

The morphological structure of wool fibres as well as the chemical composition of their proteins have been found to play significant part in the interaction of wool with metal ions. Yankasa wool fibres have large amorphous core. The cuticle of wool fibres have been shown by Hock and McMurdie[7] to be composed of an amorphous protein with comparatively cross linked intermacro-fibrillary materials. Crewther and others[5] have also shown that the cortex which constitutes a greater part of the fibre contains microfibril-matrix in the paracortex that stains heavily with metals as a result of the heavy crosslinks with disulphide bonds. It is therefore likely that the medulla, the cortex and the cuticle are centres that stain with metal ions during the treatments undertaken. Mercer[79] and Thorsen[80] have explained that the interaction of Cu^{II} and Cr^{III} with wool was due to complexing of the metal ions with tyrosine present in greater extent in the orthocortex. This appears to find support from table 4.3. III which showed the lowest moisture regain value for copper ion treated wool. Since the -OH of the tyrosine side chain is utilized in complexing with Copper ion, there should be lesser tendency for wool fibres so treated to regain moisture on exposure.

The binding of Cu^{II} ion to wool has also been associated with the coordination between the metal ion and the carboxyl group of the wool protein[81]. The result obtained from the pH change with treatment in tables 4.6. VII-IX showed that the metal ion uptake depends to some extent on the concentration of the metal ion and the number of availbale reactive sites. This was confirmed by the fact that deeper colour was observed when equal weights of wool were treated with increasing concentrations of copper II chloride solution. Since the complex formed was relatively stable, it is possible that linkages involving NH, OH, and phenolic groups may occur thus reinforcing the already operative bonds within the fibre. These views find support from infrared studies of Yankasa wool treated with copper II ion shown table 4.7.XI.

The IR spectrum of native Yankasa wool in fig. 4.7.9 showed definite absorption peaks (table 4.7.X) at 3300 cm^{-1} due to NH, NH_2 stretching, with hydrogen bonding; a peak at 2950 cm^{-1} due to O-H vibration with hydrogen bonding[82]; a peak at 1700 cm^{-1} due to CO link in COOH as proposed by Klotz and Gruen[83]. The peak at 1670 cm^{-1} which degenerated into multiplets represent stretching due to unbonded CO. It is also possible that this low CO frequency in the peptide link may be as a result of some resonance contribution of form $-OC-NH^{+}$ in the electronic structure of the group. The peaks between 1560, 1540 cm^{-1} represent N-H deformation of the amide component of the amino acid. It is also possible for carboxylate ion to show peaks around this range due to stretching and asymmetry.

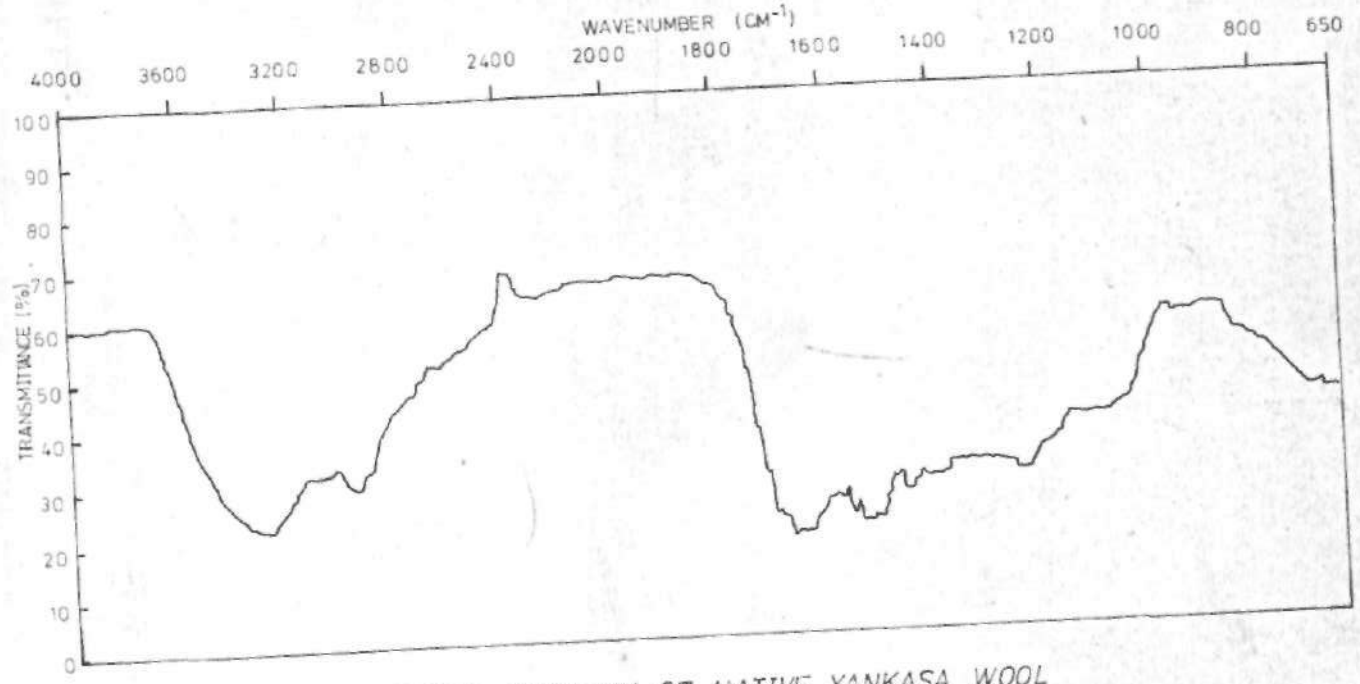


Fig.4.7.9 INFRARED SPECTRUM OF NATIVE YANKASA WOOL

Fig.4.7.10 INFRARED SPECTRUM OF ESTERIFIED UNABSORBED YANKASA WOOL

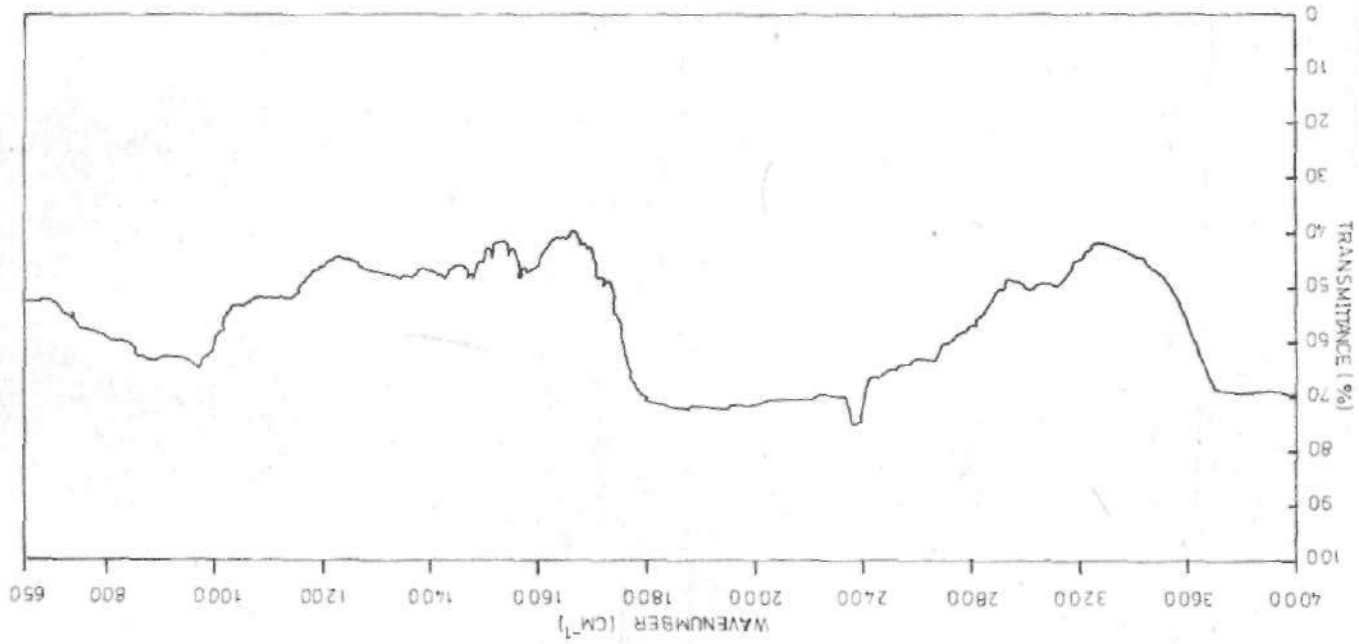
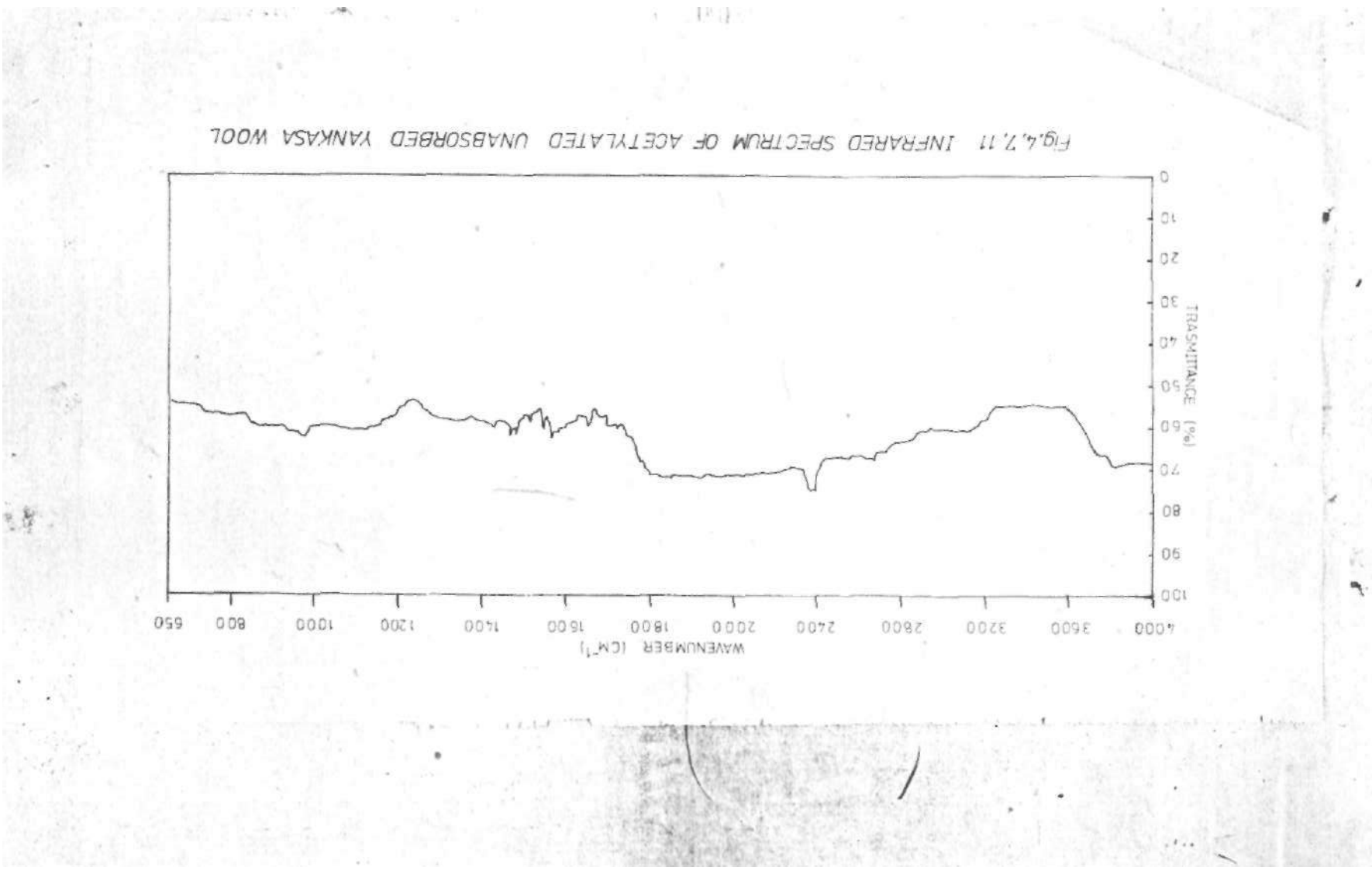


Fig.4.7.11 INFRARED SPECTRUM OF ACETYLATED UNABSORBED YANKASA WOOL



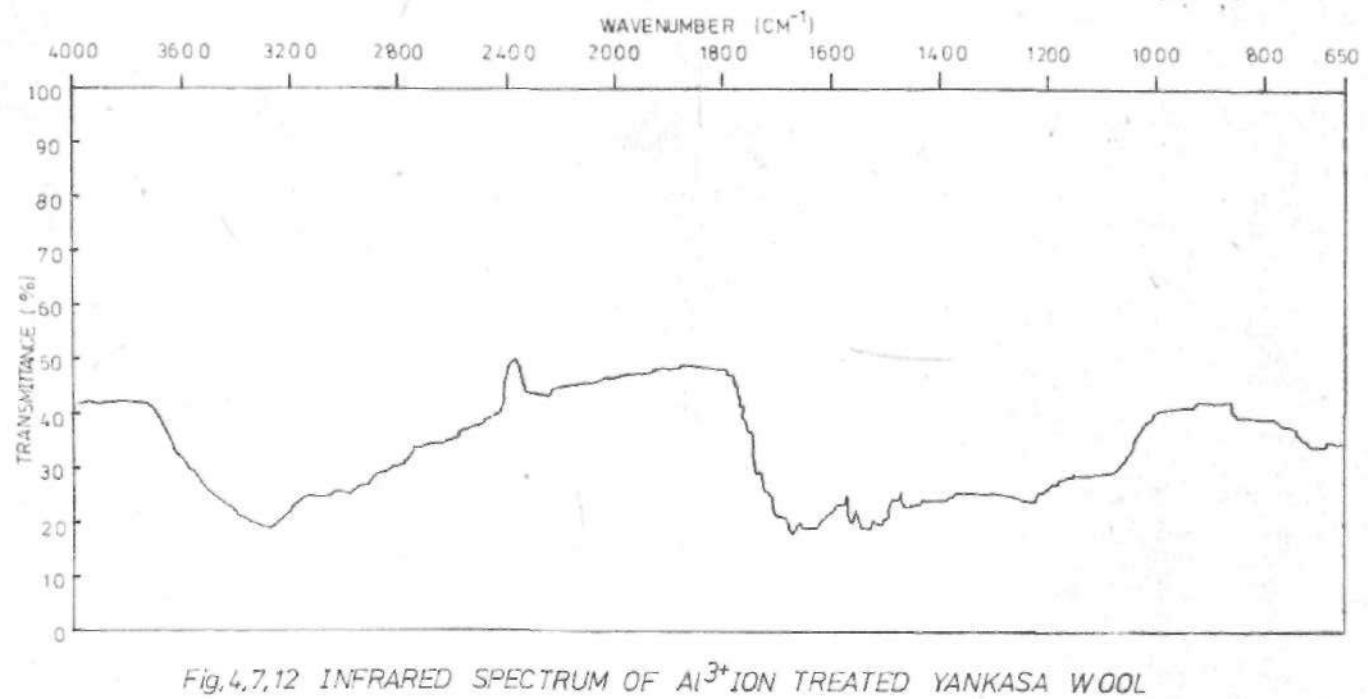


Fig.4.7.12 INFRARED SPECTRUM OF Al^{3+} ION TREATED YANKASA WOOL

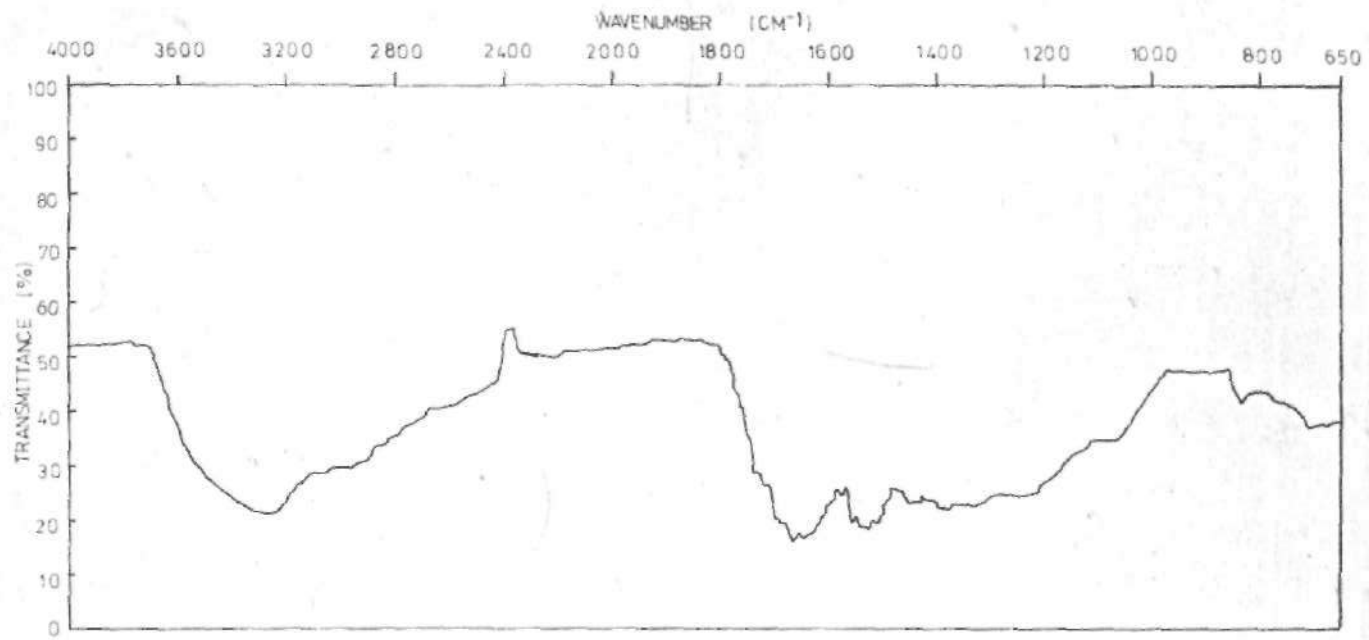


Fig.4,7,13 INFRARED SPECTRUM OF Cr^{3+} ION TREATED YANKASA WOOL

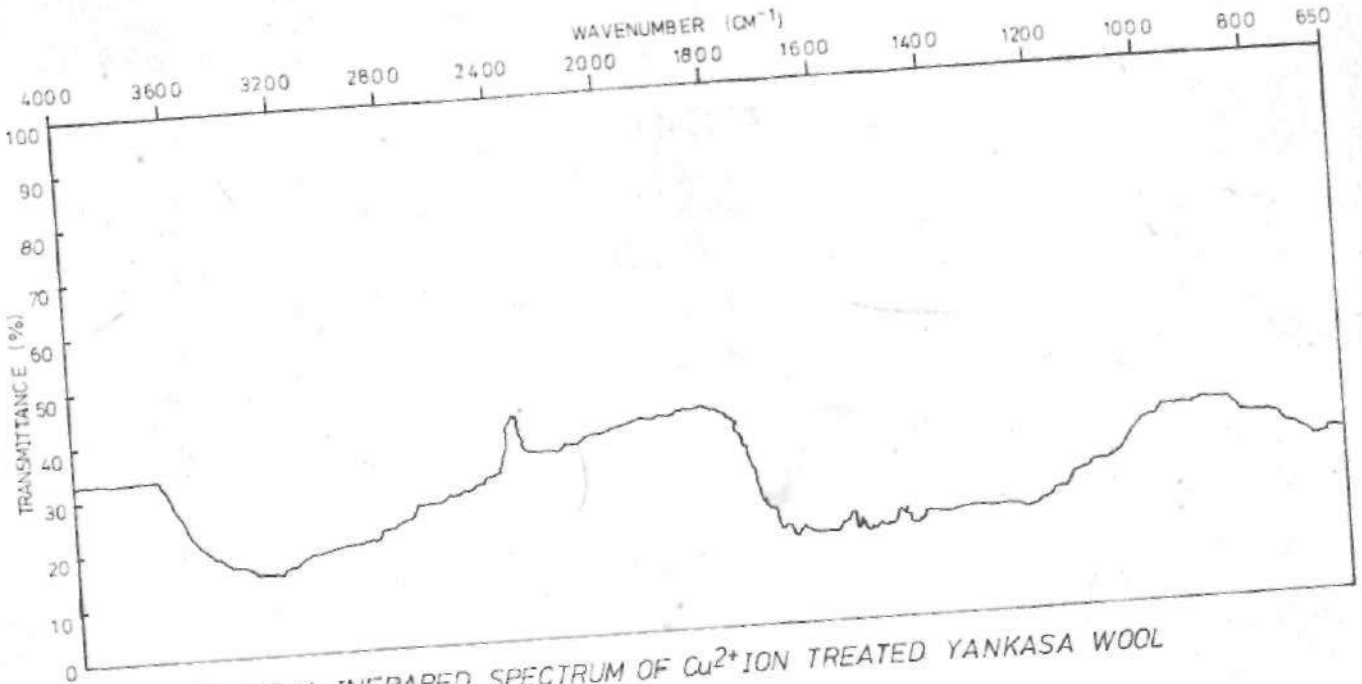


Fig.4.7.14 INFRARED SPECTRUM OF Cu^{2+} ION TREATED YANKASA WOOL

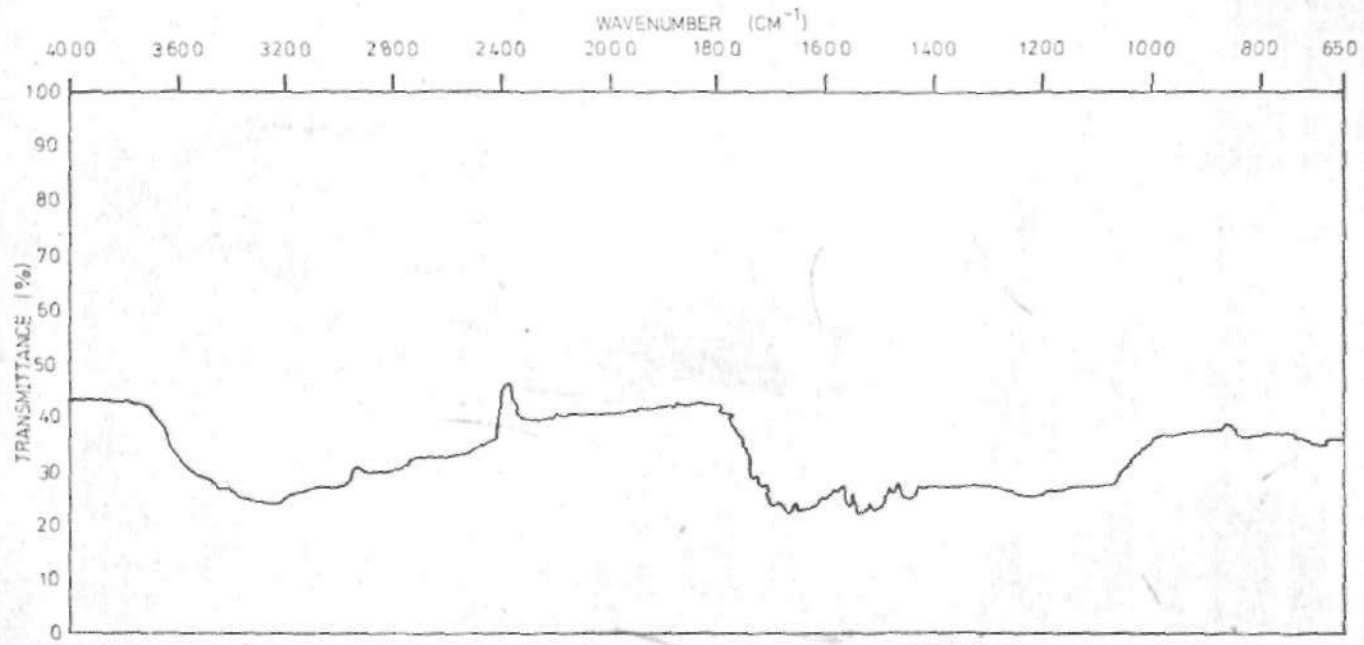
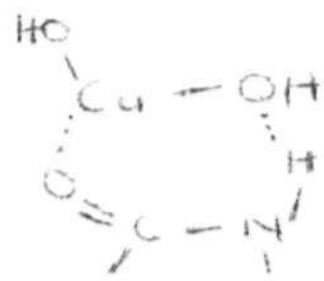


Fig.4.7.15 INFRARED SPECTRUM OF Ce^{3+} ION TREATED YANKASA WOOL

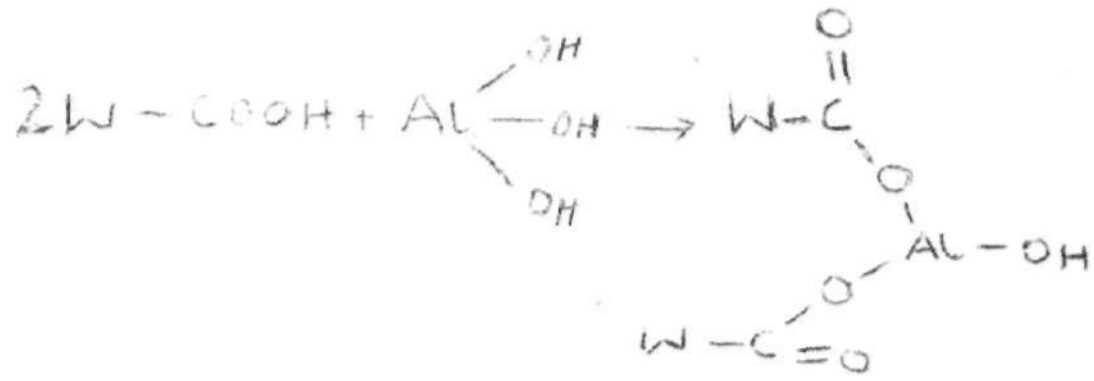
This has been confirmed by Davies and Sutherland[84] who assigned an absorption peak near 1565 cm^{-1} to carboxylate ion, and Thompson et al.[85] who found that peaks near 1587 cm^{-1}, common to all amino acids are due to carboxylate ion.

The spectrum of Yankasa wool fibres treated with Cu^{II} ions in fig. 4.7.14 showed a very broad and shifted peak at 3250 cm^{-1}. The peak present at 2950 cm^{-1} in native wool is absent. This suggests that interaction has taken place between Cu^{II} ions and the hydroxyl groups which show peaks at this frequency. This conclusion agrees with the lower moisture regain value for copper chloride treated wool in table 4.3. III and confirms the high copper II ion content absorbed by wool shown in tables 4.4. IV and 4.4. V. The spectrum indicates strong coordination resulting from interaction between Cu^{II} ions and the peptide groups on one hand, and the hydroxyl and carboxyl groups on the other. This view is in line with the structure below



Put forward by Sanger[86] to illustrate Cu^{II} ion coordination to proteins.

The reaction between aluminium and wool may have involved coordination between aluminium ion as aluminium hydroxide and the carboxyl groups of glutamic acid. During such reaction, unstable linkages of type



proposed by Atkinson and Speakman[87] may be formed. Since the linkage is unstable, it tends to agree with small content of aluminium ion obtained during the absorption experiment shown in table 4.4.IV. This unstable linkage also finds support in the infrared spectrum of aluminium ion treated wool shown in fig. 4.7.12.

The spectrum shows a set of peaks (Table 4.7.XI) at 1674, 1560 cm^{-1} with expanded area suggesting weak bonding due to vibration from the carboxylate ion. The absence of a peak at 2950 cm^{-1} suggests a binding site involving OH group and aluminium ion. There is no binding between Al^{3+} ion and NH, NH_2 groups since these groups showed defined peaks at their characteristic frequency 3270 cm^{-1}.

Chromium ion forms coordination linkages with the side-chain carboxyl groups of wool proteins which stabilizes and blocks the hydrophilic groups. This contradicts the result of moisture regain in table 4.3.III to some degree since we expect a much lower value for the regain than even Cu^{II} ion. Also the absorption

value for chromium ion in table 4.4.IV is highest so we have to seek for explanation elsewhere. The infrared spectrum of chromium ion treated wool in fig. 4.7.13 shows perturbed peaks between 1700-1600 cm^{-1} due to CO of the Carboxylate ion. This perturbation suggests binding sites. There is a shifted peak at 3250 cm^{-1} due to NH, NH_2 stretching vibration suggesting minor binding. The shape of the spectrum compared with that of native wool suggests that the uptake of chromium ion reorients the wool structure resulting in better resolved peaks. It could also be that B-pattern structure is formed with metal ion uptake.

Infrared spectrum of Yankasa wool treated with cerous sulphate shown in fig. 4.7.15 gave a broad peak at 3200 cm^{-1} and no definite peak at 2950 cm^{-1}. The moisture regain value is high and the uptake of Ce^{3+} ion by wool is low as shown in table 4.4.IV. These suggest that interaction occurs between Ce^{3+} ion and the hydroxyl and carboxyl groups of wool protein. Since the peak at 3200 cm^{-1} is relatively smaller than in native wool, it is proposed that this interaction may have resulted in some form of contraction. Structure (c) in section 3.4 of page 21 appears to apply appropriately here.

In esterified wool, the IR peak (fig. 4.7.10) at 3300 cm^{-1} due to NH, NH_2 is reduced in area while the peak at 2950 cm^{-1} is smaller than in native wool and shifted to 2940 cm^{-1}. It is likely that there is a partial blocking of the amino and hydroxyl groups during the modification[67,68,69].

This view agrees with reduced uptake of metal ions by modified wool shown in table 4.4.IV. The peaklets around 1700 - 1600 cm^{-1} are due to CO bonded and unbonded vibrations resulting from the carboxylate ion and peptide linkages proposed by Thompson et al[88]. The peak at 1688 cm^{-1} is shifted and is due to carboxylate ion. It appears from the shape of the spectrum and the appearance of peaks due to carboxylate ion that the esterification carried out on sample was minimum. The multiple peaks between 1575 - 1540 cm^{-1} are due to NH deformation.

In the acetylated wool, the IR peak (Fig. 4.7.11) occuring between 3575 - 3250 cm^{-1} is flat and broad and is due to effective blocking of the amide and amino groups. The shape of the spectrum is considerably reduced as the degree of acetylation is high. The peak at 2950 cm^{-1} is almost absent showing that the -OH group must have been modified. This agrees with the findings of Leon[64] who proposed that prolonged acetylation blocks the N-terminal groups of E-amino groups as well as the hydroxyl groups of serine, threonine and tyrosine.

Finally, the absorption data in Table 4.4.IV shows that the uptake of metal ion decreases considerably from native to modified Yankasa wool. This view is in line with the observations of Holt et al.[67] and Crewther[89] who proposed that modification leaves a net positive charge on wool fibres. This is reasonable since a net positive charge on fibre is likely to repel metal ions resulting in lower metal ion content in modified fibres obtained in table 4.4.IV.

Mechanical Properties

It was expected that the tensile strength of Yankasa wool fibres will be improved by treatment with metal ions having the ability for coordination with reactive sites in wool. The tensile strength result shown in table 4.5.VI indicates that there is an increase in strength from native to modified wool. This increase is maintained in the wool treated with Cu^{II} and Ce^{III} ions but fell slightly in esterified wool treated with Cr^{III} and acetylated wool treated with Al^{III} ions. The low tensile strength in Cr^{III} treated esterified wool may have resulted because the carboxyl group is fairly a specific binding site for Cr^{III}, while the amino and hydroxyl groups may posses higherafinity for Al^{3+} ion.

The breaking extension results show that the absorbed metal ions are acting as plasticiser in wool. This appears to be confirmed by the general increase in breaking extension from native wool to metal ion treated wool. This increase is also true for thoughness. The modulus decreased with metal treatment except in the case Cr^{III} absorbed wool. It appears therefore, that bonding involving Cr^{III} and wool proteins is stronger than is anticipated. Table 4.4.VI also shows that modification to some extent improves breaking extension of wool. This appears to conflict with reduced metal ion and dye uptake by modified wool which is also given in the same table.

Displacement of Protons from wool

The pH change during the treatment of wool with metion ion Table 4.6.VII-IX indicates that protons were displaced from wool when the metal ions were absorbed. This trend was observed in all cases of the concentration ranges (100, 200, 300, 400, 500, 1000 ppm) of metal ions considered.

In the case of Al^{3+} and Cr^{3+} ions the metal ion overtakes the hydrogen ions as the contact time increase from zero to 24 hours. However, in the case of Cu^{II} ions, hydrogen ions overtake the metal ion in the concentration ranges considered. This explains the little or no absorption of Cu^{II} ions from low metal ion solutions and short contact time.

Conclusion

Metal ion interaction with native Yankasa wool generally involves a coordination reaction between the metal ion and the active groups (carboxyly, amino, hydroxyl groups). During such reactions, the active groups act as ligands which donate electron pairs to the metal ions to form coordinate bonds. This property renders wool suitable for removing toxic and costly metal ions from aqueous solution. Chemical modification alters the charge balance within the fibre and will perhaps produce corresponding changes in ion affinities of the remaining charged functional group. This invariably results in low metal ion uptake. The uptake of metal ions strengthens the cross-linkages in the wool, thus giving a higher tensile strength and higher extension required for engineering applications.

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