SOME PHYSICAL AND CHEMICAL PROPERTIES OF

NIGERIAN MERINO, YANKASA AND CROSS MERINO WOOLS.

A DISSERTATION SUBMITTED TO

The Ahmadu Bello University

FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

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DEPARTMENT **OF CHEMISTRY April,** 1973
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A C K N O W L E D G E M E N T

I wish to express my most sincere gratitude to Professor A. R. Mathieson, Ph.D., F.R.I.C., F.R.S.A., O.B.E., Head of Chemistry Department and Deputy Vice-Chancellor for his inspiring guidance, helpful discussions and precious time devoted, throughout this work, despite his demanding duties as the Head of the Department and Deputy Vice-Chancellor.

I also wish to place on record my appreciation and thanks to Professor C.S. Whewell, Head of Textile Industries Department, University of Leeds and Dr. J. Sikorski, Reader, Textile Physics Division also University of Leeds, for kindly granting permission to work on In-Stron instrument, projection microscope and infra-red spectrophotometer.

I am also grateful to Wool Industrial Research Association, Leeds, for the Amino acid results and Mr. Brook from Textile Physics Division, University of Leeds for infra-red results.

I wish to thank my wife and children for their cooperation, constant encouragement and help without which, this work would not have been accomplished.

All members of Technical Staff of Chemistry Department (A.B.U.) deserve my gratitude for their cooperation and technical assistance. I would also like to thank Mr. A. K. Jimoh of Faculty of Evironmental Design, Mr. Amedu of Geography and Mr. J. O. Aina of Chemistry Department for their help in making the copies of graphs and typing the thesis.

I am also grateful to Ahmadu Bello University, Zaria for permission and facilities to carry out this work.

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(ii) Photographs of Cross-section of Merino, Cross, Yankasa and Baluchi wools.

A B S T R A C T

The physical and chemical properties of Nigerian Wools have been throughly investigated. Initially three wools Nigerian Merino, Cross Merino [Nigerian Merino $\frac{3}{8}$ + Yankasa $\frac{5}{8}$] and Yankasa wool were used.

The entire work has been dividied into six Chapters. The surface and cross sectional studies ~~has been~~ were made through the light microscope which reveals the difference in the scale pattern of these wools. Medulla was noted in cross and Yankasa wools. Besides these wools, two more varieties: Baluchi and Wensleydale wools have been considered. Photographs of the cross-section of these five varieties were obtained.

In the second chapter the amino acid composition of these wools has been described. Each determination was performed on the Technicon Automatic Analyser model No. 1.

Chapter three describes a study of the elastic properties of the wools. The study is confined to first three varieties, although other two wools have also been investigated but not reported. In normal operation, fibres were extended 20% and the work to stretch, work recovery and work index were obtained. The fibres were immersed completely inside the various solvents, e.g., water,

formic acid, HAC, HCl, Thioglycollic acid, alcohols, phenol, formamide and M^{2+} ions etc.; and the work to stretch 20% extension measured. The effects of the humidity, water treatment, time and temperature on the elastic properties were studied. The Hookean stress, breaking stress and breaking extension of the fibre inside different media at constant rate of loading have been investigated. Comparison of work to stretch and work recovery at constant (20%) extension for three wools have been made. The relation of work to stretch to cysteine content of these wools under similar conditions was obtained.

In the fourth chapter, the swelling properties of these wools in the presence of different solvents have been described. In solvents the fibreshave little tendency to swell longitudinally because of restraints imposed by both the amorphous and the crystalline phases. The percentage radial and volume swelling have been found. The effect of concentration upon the properties of swelling of fibres were investigated.

The next chapter presents the acid base titration properties of wools. The polyelectrolyte theory of Mathieson and Whewell has been applied to the data obtained during tne study of acid combining capacity of wools. Tne characteristics of acid-base titration curves and pK_o values for the acid titration of wool have been calculated. A theory of metal binding and metal hydrogen

exchange for wool fibres have been evolved with the support of data. Metal binding (Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}) of divalent cations has been studied in presence of acid. Investigations have also been made at different ionic strength.

Chapter six consists of some of the results of infra-red spectroscopy. The study was made for virgin wool and metal treated wool (Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}). In order to support the metal-hydrogen exchange theory, the effect of metal ion on the absorption peaks thoroughly studied.

Some other physical properties such as, measurement of birefringence, and cross sectional and surface structure have been studied and presented in the appendix.

Chapter 1

I N T R O D U C T I O N

1.1.0 SHEEP

No farm animals have so many breeds evolved as a sheep. Many of these breeds are of little importance in commercial production, with more than three fourths of the industry of the world based on the use of not more than six breeds.

Breeds of sheep may be classified on several different bases, including:

(1) Their degree of suitability for mutton or wool production (mutton or wool type).

(2) Colour of face (white or black face).

(3) Presence or absence of horns (horned or polled).

(4) Topography of the area in which they originated (mountain, upland, or low land), and

(5) Type of wool they produced.

The latter classification is perhaps the most suitable.

The following are the leading breeds of sheep:

Fine wool type	Medium wool type	Long wool type	Cross level type	Carpet wool type	Few type
Merino	Cheviot	Cotswold	Columbia	Black	Karakul
Deboiult	Dorset	Leicester	Corriedale	faced	
Delaine Merino	Hampshire	Lincoln	Panama	highland	
Rambouilt	Montadale	Romey	Romeldale		
Targhee	Oxford		Targhee		
	Ryeland				
	Shropshire				
	Southdown				
	Suttolk				
	Tunis				

1.1.1 Fine Wool Breeds

The most common fine wool breeds of the world is the merino. There are different breeds of merino, but all of these breeds, the spanish breed, is the finest one. No breed of sheep has contributed so much as the merino to the development of the world wide sheep and wool industry. The Merino breed furnishes the foundation breeding to produce fine wool.

The word merino is derived from an early-day royal officer of spain, called Merino, whose duty it was to assign the various migratory flocks of the country to their respective grazing grounds. In its native land, the Merino breed of sheep had long been selected for fine wool and strong flocking instincts.

Four Main Migratory Sheep

Escurial Type	Finest, very beautifully crimped.
Paular Type	Soft, close and compact.
Negrette type	Short, skin large and folded big animal, rams had very large horn.
Infantado type	Similar to Negrette, ram's horn more closely set.

1.1.2 Origin of Merino.

There have been fine woolled sheep in spain since Roman times and sheep of the merino type were well known in Spain during and after the period of the Moorish occupation. For many years exportation of fine woolled sheep from Spain was forbidden. First significant exportation was allowed to Saxony (East Germany) in 1765, followed by another purchase in 1774. A small flock of Negrette was imported into England in 1791, but did not survive. In 1808, another flock of 2000 paular sheep reached England which were eventually settled in Victoria (Australia). The first importation of Merino into the U.S.A. was in 1802, but on large scale, 1909 onwards.

1.1.3 History of Nigerian Sheep

In 1960 - 1961, the Government of Northern Nigerian imported Merino rams from South Rhodesia. The detail accounts of the fertility, growth rates are reported by Ferguson(5882). The Merino sheep were well built, fairly plain-bodied. The fleece was coarser on the Britch but finer on to shoulder, free from kemp and pigment.

Besides Merino, there are two more foreign breeds available in the Northern part of Nigeria. They are Baluchi and Wensleydale. Baluchi sheep are from the North Western part of Pakistan. They were originally imported from Iran.

Wensleydale:

The sheep is large but not as big as Lincoln or the Leicaster. The wool is longer and slightly brownish tinge and lustrious.

The local breeds which are more common and more popular for meat production. Ouda, Yankasa, Balanu Ouda breeds are mostly maintained by the Fulani people in the North Eastern State.

The Balanu are more popular in the North Western State and Katsina province. Niger Reolublic also had produce some of these breeds (Balanu , Ouda etc.)

The Ouda and Yankasa are found in North Central State, Benue Plateau State and Kano State. These breeds are actually desert type having hairy fleece. The animals are long thin legged. Some of them are pigmented in either black, dark brown or pale brown.

But Yankasa is white. The wool is coarse but better than Fulani goat. The fibre is kempy and has medulation throughout the centre. Cross breeding between merinos and different Nigerian (Yankasa and Ouda) sheep has been carried out in many parts of the country for the purpose of mutton and improved quality of wool.

1.1.4 Grades of Wool.

Grades of wool are based on fineness. Fine wools make finer fabrics than coarse wools. Fine fabrics are more desirable and more valuable than those made from coarse wool. Grading of wool is very important because fine wool fetches more money.

The grade of wool may be given in either the American or Bradford system. These systems use very different terminology, but both are based on relative fineness of wool fibres. The American terminology originally referred to the kind of sheep from which the wool was most likely obtained. The "counts" of the English or Bradford system indicates the number of hanks of yarn spun from wool of a particular fineness that would weigh one pound, or, as it is sometimes stated, the number of hanks of yarn that can be spun from one pound of such wool in the form of top. A hank contains 1,680 feet, but wool of a given count may be spun to a different number of hanks than the count indicates.

Comparison of Two System Together with Their Length and Diameter

Bradford	American	Approximate length in inches combing	Average diameter Range (Microns) Minimum	Maximum
80'S	-	-	18.1	19.1
70'S	-	-	19.6	21.0
64'S	Fine	Over 2	21.1	22.5
60'S	-	-	24.1	25.5
58'S	Half blood	Over $2\frac{1}{4}$	25.6	27.0
56'S	Three quarter blood	Over $2\frac{1}{2}$	27.1	28.5
50'S	-	-	30.1	31.7
48'S	Quarter blood	Over $2\frac{3}{4}$	31.8	33.4
46'S	Low quarter blood	Over 3	33.5	35.1
44'S	Common	-	35.2	37.0
40'S	Braid	-	37.1	38.9
36'S	Braid	-	39.0	41.2

1.1.5 HISTOLOGY OF THE WOOL

Wool and other keratin fibres possess similar structures. The structural features to be considered in the present discussion are mainly those that are visible with the ordinary light microscope. Three main types of preparation are used to show these. The simplest is to mount the whole fibre, or a part of it, in a

medium such as liquid paraffin or glycerol. This method shows the profile of the fibre and some of the details of the cortex and particularly in pigmented or heavily medullated fibres. Casts of the fibre surface made in various thermophatic media are used to study the scale pattern of the fibre cuticle. In order to study some of the finer structure, sections of the fibre, both transverse and longitudinal, are used. (vide appendix 6)

Besides light microscopy, the x-ray technique is also very useful in studying the details of fine structure of wool. All fibrous proteins given an x-ray diffraction pattern (1,2,3) characteristic of an α - polypeptide structure which after stretching is replace by β - pattern. The reversible nature of the $\alpha \rightleftharpoons \beta$ transformation was investigated mainly by x-ray diffraction techniques, and had provided valuable information regarding the structure of both crystallographic forms. Following the work of Pauling and Corey (4), the α keratin is considered to be built up of long peptide chains arranged in the form 4 α-helices , packed in pseudo-hexagonal array. Observations by MacArthur (5) and Perutz (6) provided considerable support for this model but the strong meridional spacing of 5.15A was not accounted for. Later, the coiled - coil arrangement was proposed (7); and it appears that the structure of the "Crystalline" part of the mamalian keratin approximates roughly to that of a rope composed of two or three α-helices regularly distorted and intertwined (8).

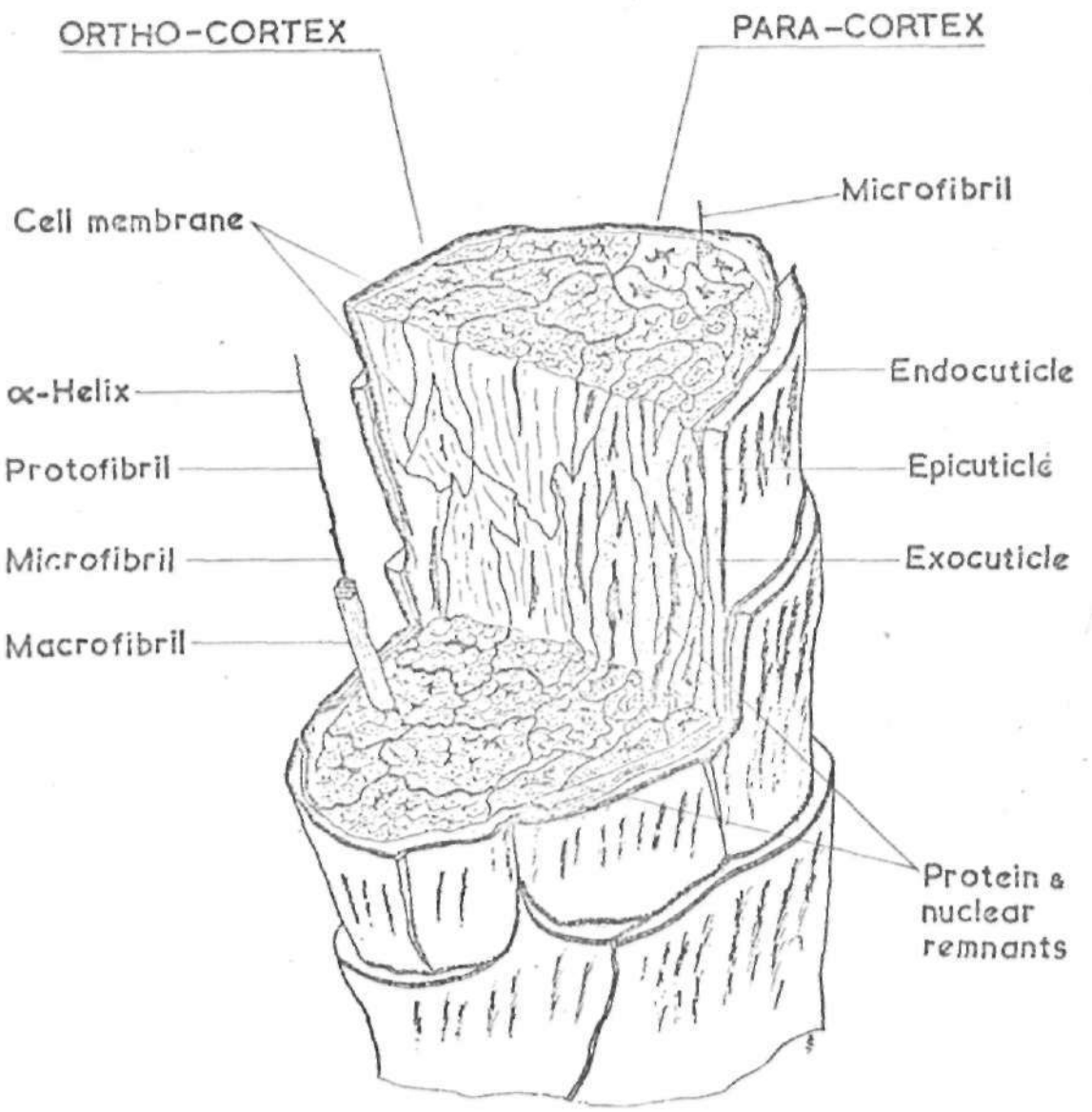


FIG. 1. Representation of a wool fibre. (Ref. 83)

These ropes or protofibrils are, in turn packed together to form micro-fibrils (9,10). The non-helical component of the low sulphur protein fills the inter-sites between the central protofibrils and the outer ring of the protofibrils (11).

Electron microscopic examination of thin transverse, and longitudinal sections of wool fibre revealed further details of surface structure.

The morphological detail of wool keratin is represented in Fig. (1) which shows the individual units present in a fine wool fibre. (Merino 64'S). The coarse fibres which consist of medulla, are mostly kemp fibre. The cross-section (Fig. 2) reveals that there are three main parts - cuticle (on the outside), cortex (inside) and medulla within the cortex. (83, 15)

Cortex

The cortex (Fig.2) comprises more than 90% of the fibre. The cortex consists of spindle shaped cells which are approximately 100 microns long and 2 - 4 microns in diameter (12,13,14) and which are arranged with their length parallel to the fibre axis and are separated by disorganised material. This material acts as a "cementing" medium between cells and further adhesion is afforded by the interlocking of cellullar projections located mainly, but not exclusively, at the cell tips. It is generally accepted that in the fibre a membrane surrounds each cell. The stability is shown in spite of the elongation of cortical cells, their position with



P — para-cortical cell

O — ortho-cortical cell

C — cuticle cell

M — cell membrane

R — cell residue

m — macro-fibril

FIG. 2. Diagram of a Merino wool cross section. (Ref 15)

respect to each other, after stretching, is apparently unaltered (12).

In crimpy wool fibres, the cortex consists of at least two types of cells (15) designated as the ortho-type and the paratype (15,16); the former always occupies a position on the outside of the natural crimp (17), but additional cells may also be occasionally observed, forming a meta or meso-cortex (13).

The ortho- and para cortical cells differ widely in both reactivity and morphology. The ortho-type cells consists of a compact assembly of macrofibrils (each approximately 1,000A' - 2,000A^{o} in diameter) and contain relatively few nuclear cell residues. The para-cortical cells are generally smaller in their sectional area and their micro-fibrils are not so densely packed. The cross sectional area of a fibre is usually divided into ortho-or para regions by an imaginary line drawn across the major or minor axis of the ellipse.

The para cortical cells are attacked preferentially by oxidising and reducing agents and are thought by some investigators to contain the majority of cystine residues (18). This belief had been contested by Ryder (19) and Leveau (20). In spite of difference in their chemical behaviour, Bones and Sikorski (21) had shown that contrary to earlier belief (22), the mechanical properties of the two types of cell appear to be similar.

Electron microscope studies of wool fibres which had been previously reduced and treated with heavy metals, have revealed,

especially in the paratypes cells, that the macro fibrils, consist of a system of filaments called microfibrils each about 75A° in diameter and surrounded by a heavily stained ground substance known as matrix (20,23,24,25). The microfibrils were seen to be arranged in layer and near-perfect hexagonal arrays in para-cortical cells while, in the ortho-cortical cells, the packing gave the appearance of lamellar or whorly arrays with microfibrils. The difference in the packing arrangement of the microfibrils was considered to be due to a better alignment of the microfibrils, with respect to the fibre axis, in the paracortical segment (26). It had been possible to sub-divide the microfibril structure due to changes in distribution of the intensity maxima in the image of metal transverse section of cortex. It was indicated (27) from the observations of negatively stained, ultrasonic disintegrated wool, that the microfibril is composed of a number of smaller units - about 20A° in a diameter, referred to as protofibrils (28,29. The protofibrils are thought to consist of molecular chain in the form of two or three α-helices grouped together.

The structure of matrix which remains largely unknown, is considered to be a less - ordered region than the microfibril. It is now generally accepted that the wool contains two main groups of proteins which differ considerably in chemical composition and physical properties. Our source of information only lies upon the

study of electron microscope evidence. The low-sulphur proteins are considered to be derived from the microfibrils and the high sulphur proteins from the matrix. More information had been provided when the denser regions (matrix) appeared in thin transverse sections of fibres reducedand treated with heavy-metal compounds indicating the site of available sulphydryl groups (30,31). It had been demonstrated, by the electron microscope that high - sulphur proteins, extracted from the oxidised wool by neutral buffer, originate, at least in part, in the matrix (32) and that wool from sheep receiving cystine supplement, show a large increase in the amount of matrix and in the intensity of matrix 'staining', compared with wools from the sheep on a control diet (33).

Orthocortex.

Fraser and Rogers (34, 35) observed, after methylene blue staining, that the degree of cortical segmentation is related to fibre diameter and not to the breed of sheep. In wool less than 25 microns diamter, the two segments are discrete, while fibres with a range of diameter between 25 - 35 microns, the demarcation is less pronounced and the orthocortex is surrounded by the paracortex and vice versa. When the diameter of the fibres is greater than 35 microns, segmentation is not apparent, although there is a tendency for the paracortex to occupy the periphery of the fibre. Ahmad and Lang (36), also using methylene blue staining - classified the fibres together on the basis of the arrangement of the two cortical

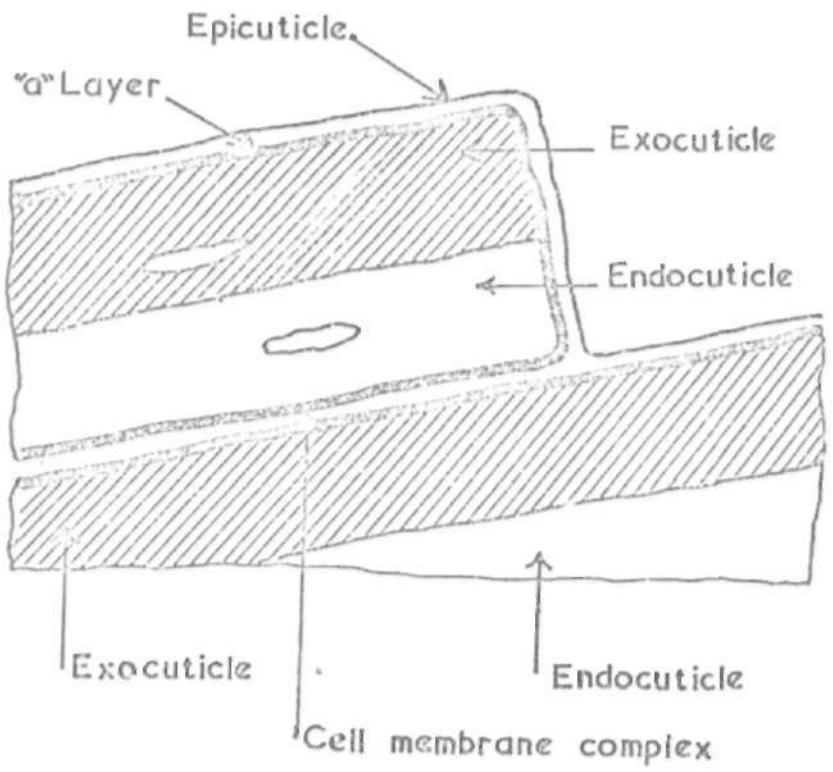


FIG. 3 A representatation of the structure of the cuticle. (Ref. 37)

segments. A clear demarcation along the major or minor axis of the fibres generally occurs in the fine crimpy wools, while coarser wools, the segmentation becomes less well-defined, due to gradations in staining of the orthocortex.

In general, the relative amounts of ortho and paracortex were found to vary between wool with the same diameter.

The Cuticle:(Figure 3)

The outer sheath of the fibre consists of a layer of flattened cells, (the scales), the edges of which overlap each other and point away from the root end of the fibre. Wildman (37) described the scale patterns for many different animal hairs, among the four main types of wool. Kemp wools are coarse, very widely medullated fibres shed annually or more often. They are obtained from the carpet wools and in the fleeces of many mountain sheep. Their scale pattern is like a regular mosaic of units often as long as they are wide. At higher length of the staple, towards the tip, the pattern is changed to an irregular mosaic with the units distinctly shorter along the fibre axis than they are in width. In the kemp fibres, both types of pattern are present, though the point of change along the fibre may differ with breed and enviroment.

In the coarss breed like Swaledale, or Devon Longwool, scale pattern is like the regular mosaic found at the base of kemps, but there may be short regions of the irregular mosaic with fairly short

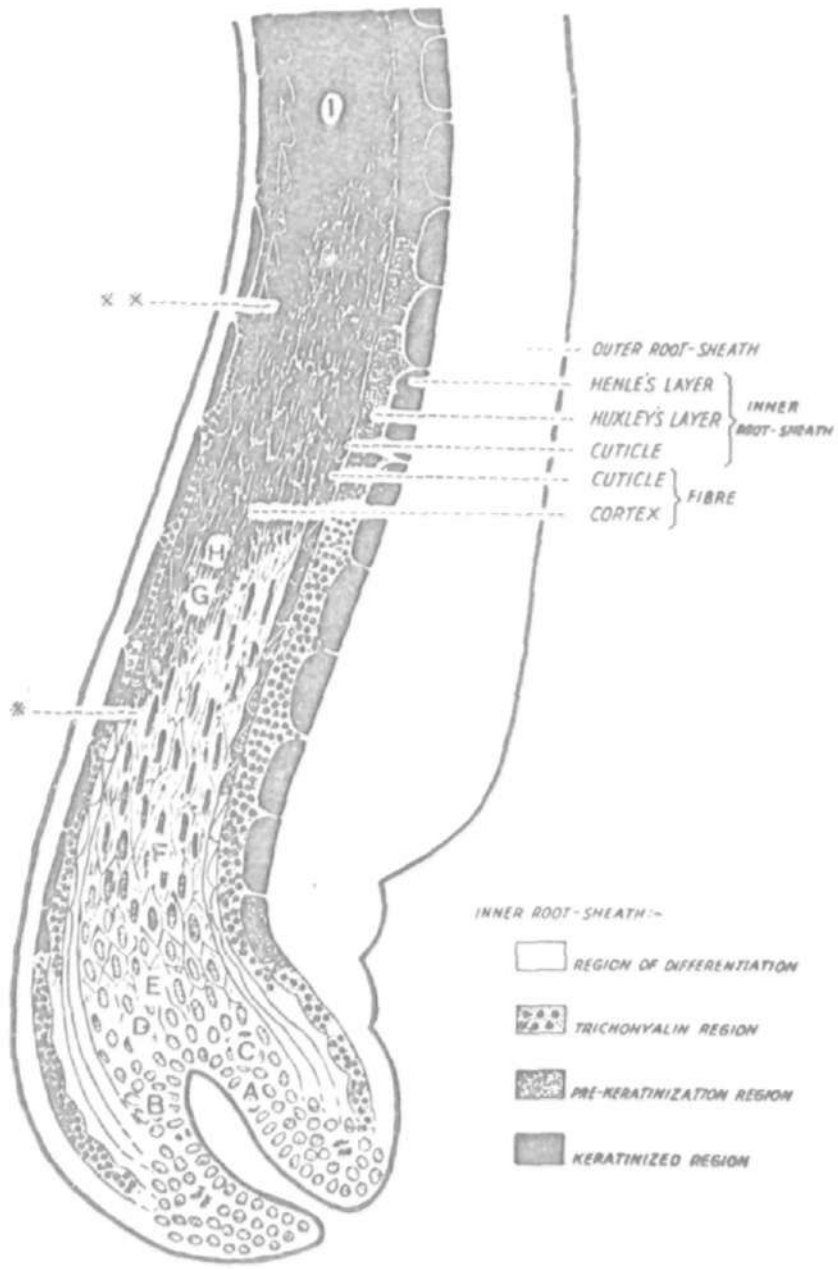


FIG.4. The development stages of keratin in the follicle.

[Auber, L., Trans. Roy. Soc., Edin., 1952, 62, 101].

scales. Very fine wool fibres have coronal scales in which a single scale envelops the fibre, but the majority of ordinary fine wools need two or more scales to lap the fibre.

Generally the cuticular cell is thicker at the distal end than at the proximal end, and furthermore. The total thickness varies in the former case from approximately 4000A° for Lincoln wool to 3000°A for Merino wool.

The individual cuticular cells are held to the fibre cortex by interlocking process found mainly in the proximal regions of the cuticular cells. Similar features have been found between the individual cuticular cells. The cuticular layer is also stabilised in part by an inter cellular medium which acts as a cement between neighbouring cells.

In contrast to the cortex, the cuticle shows little organization and contains less tyrosine but greater percentage of sulphur. The purpose and origin of the cuticle had been studied by many workers, some claiming that it is involved in the process of separation of the fibre from the inner root sheath, (38,39) others suggesting that the cells slope downward towards the root because of a difference in growth rate between cuticle and cortex. Cuticular cells are not simply a homogeneous shell, as can be seen from the (Fig.) but comprise several structurally distinct layers (epicuticle, exocuticle, endo-cuticle and a-layer).

The Epicuticle:

The epicuticle having 100Å thickness was isolated by Lindberg, Philip and Gralen (4) by treating the wool with a solution of sodium sulphide, and examined in the electron microscope. The All-worden reaction which results in the formation of liquid filled bubbles on the faces of cells when fibres are immersed in aqueous chlorine solution, was interpreted by Muller (84) in terms of the epicuticle membrane. He suggested that the chlorine diffused through the epicuticle and attacked the protein in the scales, causing osmotic pressure which resulted in the formation of the liquid filled bubbles. Epicuticle is damaged mechanically in carding and by the usual soap and soda scouring.

It is very diffucl to isolate absolutely pure epicuticle from a wool fibre (0.1% by weight). The chemical nature of the actual membrane itself is still open to considerable speculation. Zahn (41) assumed the presence of proteins, while other workers suggested (42) that the membrane was made up, predominantly or at least in part, from waxes, Gralen (43) claimed presence of carbohydrates.

A-Layer

A very thin layer, approximately 100 µm thick, is observed when metal stained sections of wool fibres are examined in the transmission electron microscope. The layer is more heavily stained than

either the exo- or endo-cuticle and is continuous around the periphery of the cell (44). The nature of α-layer is still uncertain, but it was proposed that it may contain an extensive system of disulphide linkages.

The Exocuticle:

The exocuticle layer is situated immediately adjacent to the α-layer and often occupies the complete distal end of the cell, as indicated in (Fig. 3). The exocuticle is attacked by most of the keratinolylic agents (44) but is comparatively little attacked by Trypsin. Dobbs (44) attributed this lack of reactivity to extensive disulphide cross-linking in the structure. The approximate size of the layer is 150 - 200 µm. The increase in density of the exocuticle, subsequent to 'Staining' with silver and mercury compounds, which are considered to react with sulphydryl groups, and its solubility in keratolylic reagents suggests that the exocuticle is keratinous in nature.

The Endo Cuticile:

The endo cuticle situated adjacent to the exocuticle and radially nearer to the cortex, is approximately 140 - 1000µm thick. The layer is attacked by the enzyme trypsin which can remove the layer completely. The enzyme trypsin is known for its ability to break peptide bonds, at the carbonyl ends of the amino acids arginine and

lysine, and, therefore, it supports the view that large amount of these basic amino acids are present in the endo-cuticle. The differences in density of the exocuticle and endocuticle layer appear to vary with the type of staining compound used. When silver or mercury compounds are employed, generally, the exocuticle appears more dense than the endocuticle, the reverse situation occuring when uranyl salts or phosphotungstic acid are used. The absence of reactivity between uranyl acetate and cystine linkages indicates that endocuticle is probably poorly cross-linked.

Medulla

Air filled network of membranes situated in the centre of many coarse wool and hair fibres are known as medulla. Whenever undyed fibres mounted whole in liquid paraffin or glycerine are examined in the microscope the medulla appears dark, but if very shot pieces of fibre are mounted the medium enters the medulla and the contrast almost disappears. The membrane continuous or broken is best seen from cross sections of very coarse fibres. The nature of medulla differs from breed to breed. Few Mohair fibres are medullated, whereas most alpaca and Ilama fibres contain two channels of medulla. The formation of medulla is strongly inherited (45,46), but it is also affected by climate and food. Medullation is not common in wools finer than 50^{s} quanlity, but all coarse wool fibres are not always medullated. It is interesting to note that fibres which appear non-medullated in the light

microscope often exhibit the above structure when examined by polarized light (47). In the extreme case of kemp fibres, the major portion of the cross-sectional area is made up of medulla (48) which contributes the increased brittleness, giving rise to typical fractional properties (49). Auber (50) reported that medulla of mature fibre is composed of large "empty" cells, which may be partially keratinised, permeated throughout by large intra - and inter-cellular air spaces. The medulla contains less sulphur than the rest of the cortex, although it is resistant to attack by keratinolytic reagents (51). Stoves (52) claims that there is a fine membrane, containing lipid, protein and cholesterol, covering the surface of medulla cells, while other workers (50,53) had found granules and white pigment in the medulla. (vide appendix - Yakasa)

1.1.6 Molecular Structure of Wool Keratin

1.1.7.1 Structural Models of α-Keratin

It is now generally accepted that α-helix suggested by Pauling and Corey (54,55) ~~which they expressed the belief~~ that a spiral configuration of the polypeptide chain was present in (4) α-keratin. α-helix structure is based on a trans-planer amide group and containing 3.6 amino acid residue per turn, forms the basic Structural Unit of keratin. Confirmation of the structure of the α-helix was obtained directly from x-ray diffraction studies

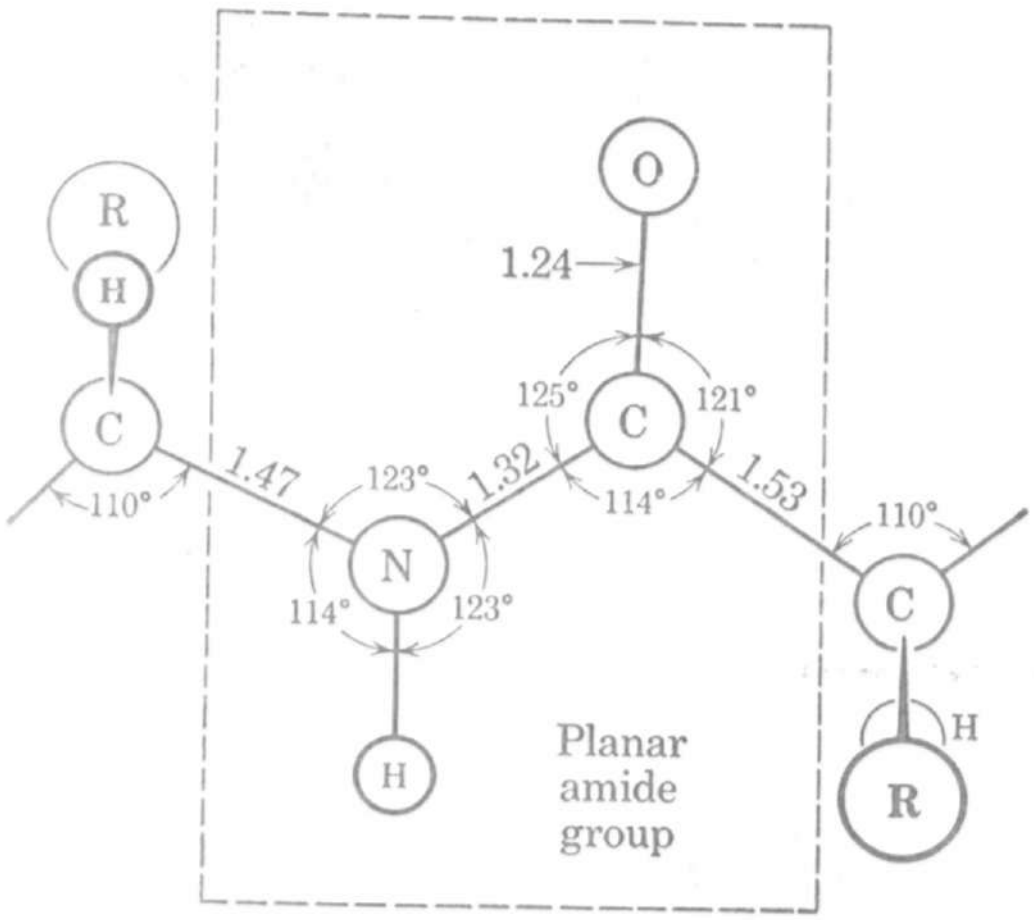


FIG. 5. Fundamental dimensions of polypeptide chains as derived from x-ray analyses of amino acids and simple peptides [from R. B. Corey and L. Pauling, Rend. ist. lombardo sci. **89**, 10 (1955)].

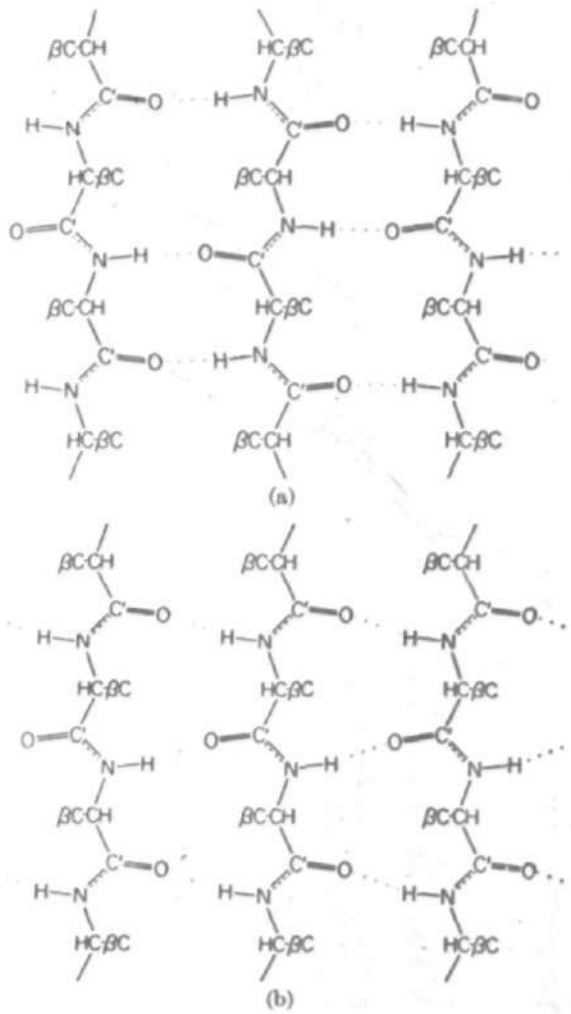


Fig. 6. Diagrammatic representations of the two pleated sheet structures proposed by Pauling and Corey (4, 55) (a) The anti-parallel pleated sheet, with chains running alternately up and down. (b) The parallel pleated sheet, with all chains running in the same direction.

Pauling and Corey, (1951). Proc. Nat. Acad. Sci. USA., 37, 205

of synthetic polypeptides, particularly poly-γ-methyl-L-glutamate (56,57) and poly-γ-benzyl-L-glutamate (57,58,59). The work of Kendrew (60,61,62) on myoglobin provided not only direct proof of the existence of the α-helices in protein but showed also that the length of the helical segments does vary depending upon the amino acid side-chain reaction. (Fig. 5,6).

α-helix embraces two distinct structures which for L-amino acids involve coiling eitner into a right-handed helix, corresponding to β-carbon atom.

The earliest model of α-keratin structure based on the α-helix was that of Pauling and Corey (55), who suggested that α-keratin contained α-helices packed in pseudo-hexagonal array. The Pauling and Corey's proposed model is based on the following parameters:-

(i) each amino group is planer, to account for the resonance of the double bond in the peptide link, with the C=O and N-H groups in the trans-configuration.

This is considered the most stable configuration since any departure by more than ten degrees from the planer configuration would result in instability (54,55)

(ii) All amino acid residues are equivalent except for side chain differences.

(iii) A hydrogen bond system is formed between C=O and N-H group.

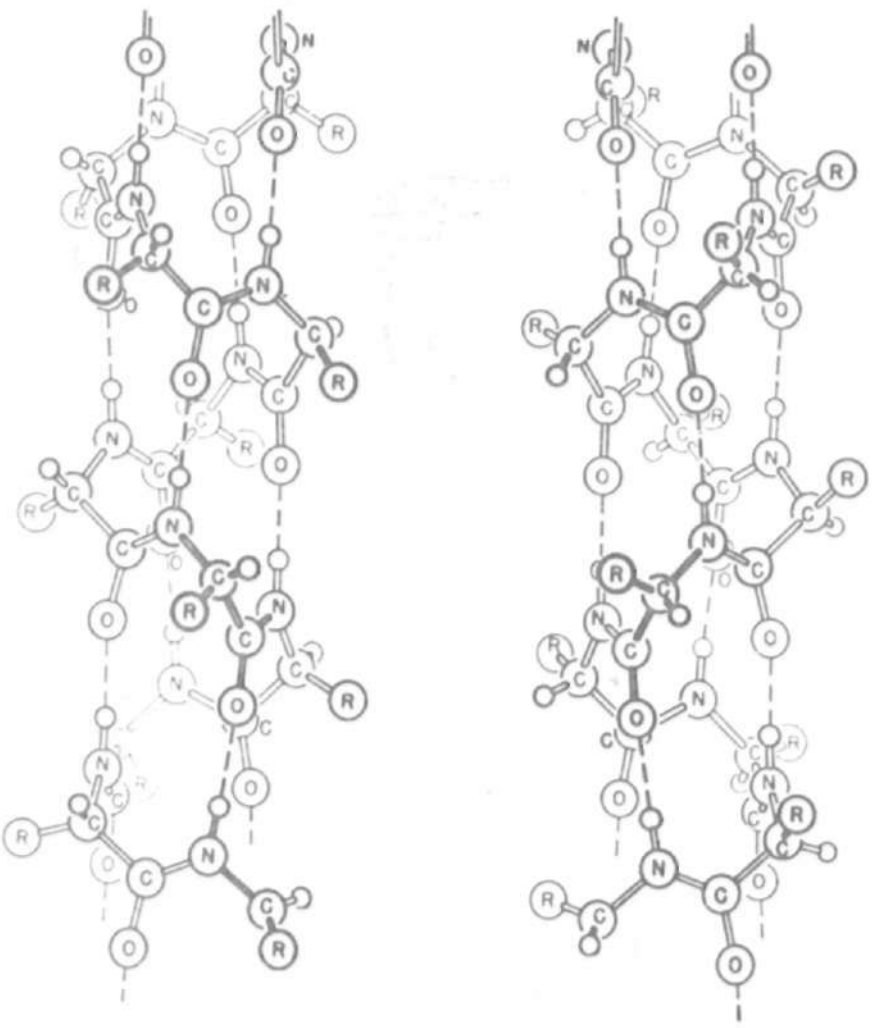


Fig. 7. The α-helix; left-handed (left) and right-handed (right). All residues are L-amino acids (Ref. 55, 62).

Corey, R. B. (1938). J. Am. Chem. Soc. 60, 1598

Two hydrogen bonded spiral polypeptide chain were proposed on the basis of the above parameters, (a) the α-helix (62) comprised of 3.7 residues per turn and (b) the γ helix of 5.1 residues per turn, considered representative of super-contracted keratin. The pitch of the α-helical configuration is 5.4A and the rise per residue is due to inter chain hydrogen bonds lying parallel to the axis between the -NH and -C=O of adjacent turns. (Fig. 7)

The Coiled Coil

A coiled-coil system proposed by Pauling and Corey (55) was based upon repeating sequences of seven amino acid residues forming major helices, with either 190A or 400A pitch. Two types of super-coils were suggested: a "three-strand" rope consisting of three helices, with 190A repeat, and a "seven-strand" cable formed by six, 400A pitch helices surrounding a single "straight" α-helix to give a "rope" of diameter about 30A. (Fig. 8,9), Although this wool model accounts for several features of the x-ray photograph of α-keratin and gives reasonably good co-relation between observed and calculated densities, it does not explain the low-angle equatorial reflections and, furthermore, contradicts the electron microscope evidence.

A discontinuity in a coiled coil system should not be ruled out due to complex side-chain interaction. Most of the evidence

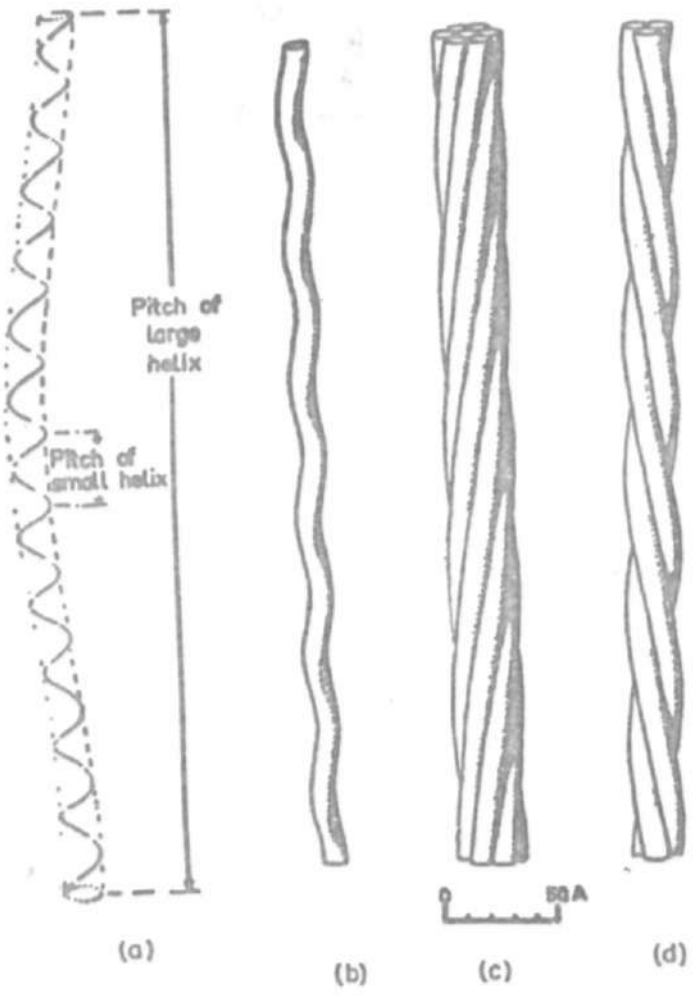


Fig. 8. Illustrating the compound helix (a) and (b), the seven-strand cable (c) and the three strand coiled-coil (d) (Ref. 55).

Pauling and Corey (ref 53).

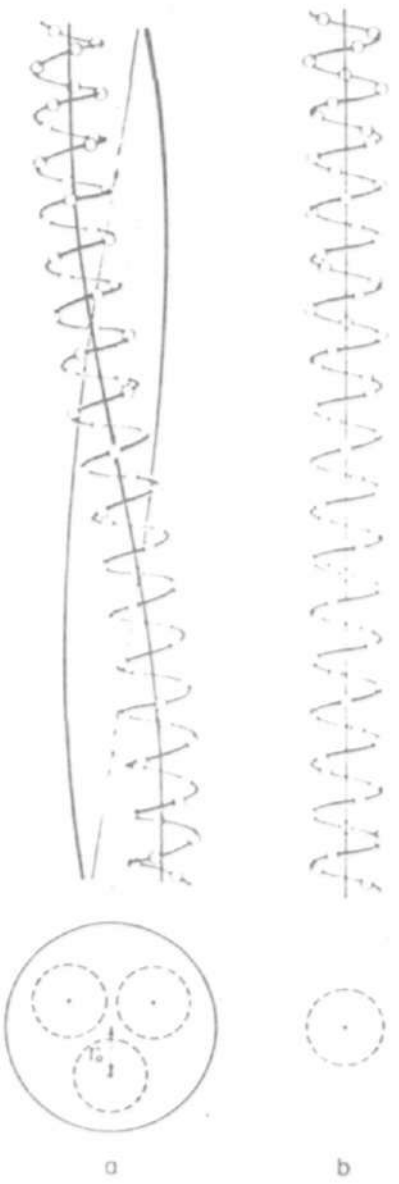


fig. 9 (a) Distribution of residues in the three-strand coiled-coil rope. For clarity, only one coiled-coil is shown. (b) Distribution of residues in an undistorted α-helix. (Ref. 55).

From. Crick, F.H.C. (1965), Nature, 170, 882.
and from Advances in Protein Chemistry Vol. 20
Acad. Press. N.Y., 1965. page 294.

obtained from protein solution studies, infra-red methods (63 , 64, 65,66) and amino acid analysis (67) showed that the formation of helical peptides was not favoured by the sequences including the amino acids which have hetero-atom attached to the β-carbon atom, e.g., serine, threonine, cysteine and proline, and those which branch at β-carbon atom, (Valine and isoleucine). Similarly, the amino acids with large side chains such as aspartic acid, phenylalamine, have a tendency to discrupt the helix conformation.

β Keratin

Most established configurations of β-keratin are two which satisfy Pauling and Corey's criteria for stability, an anti parallel chain pleated sheet of 7.00A, and a parallel chain pleated sheet, with a repeat of 6.50A (Fig.6) (68).

The most detailed information on the β-structures in keratin, originally reported by Astbury and Street (69,70) in stretched hair and wool, has been obtained from specimens extended and pressed in steam, showing double orientation, namely, with the "side-chains spacing, normal to the plane of flattening, and the "back-bone spacing" parallel to this plane. Fraser and Macrae (71) re-investigated the x-ray diffraction data obtained by Astbury and Sisson (70), using stretched and pressed horse hair, and concluded that a mixture of both parallel and anti parallel chains are present in keratin. It was considered most likely that the chain direction would, to a

certain extent, be pre-determined, since the chains in any one "β-crystallite could be considered to originate from the same "microfibril".

α → β Transformation.

Many
~~Much~~ details have been obtained regarding the fine structural organization of wool during the dimensional and crystallographic modification (1, 3, 73). A characteristic x-ray diffraction pattern of the α-type obtained from the virgin wool fibres, is transformed into the β-configuration (74) after stretching up to 10 percent in water, at 20°C, or even 120 percent, in steam. The transformation is reversible at low temperature, although a weakening of the (Fig. 11) meridional reflections become evident (75), but at higher temperature (above 40°) irreversible modification of the structure occurs. Skertchly and Woods (76,77), using Geiger counter diffractometer technique, have indicated that the molecules in the β-configuration may be detected at about 5 percent, or even lower extensions, and that the transformation is not complete until 100% extensions.

Bendit (78,79,80) proposed, on the basis of disappearance of typical α-pattern and emergence of β-reflection, an intermediate phase in the transition. He suggested that the α-helices are first stretched into a more "random configuration", whilst β-material formed in the early stages originates from the presence of (Fig 11) "non-crystalline" material. Skertchly and Woods (77) recognised

the presence of an intermediate (β') phase, appeared to reach maximum at 50 percent extension, but suggested that, since the β- phase is merely indicative of an intermediate state of organization, the idea of "non-crystalline" material transformed to the β-configuration was unnecessary.

In order to explain the molecular transformation process, Turner and Woods (81) assume that the amount of α-material present at zero percent extension is approximately the same as the amount of β-material present at 100 percent extension. Though this assumption seems to be justified for a system of long molecular chains, but such a simple relationship may not necessarily apply to the complex structure in keratin.

There is little information available about the fat of microfibril during the coarse of the α-β transition.

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2.0 AMINO ACID COMPOSITION

A considerable amount of information is available concerning the amino acid composition of different wools. Table 2.1 (1,2).

Many peptides in wool hydrolysates have been identified and their composition established. (3,4). Simmonds (5) used manual chromatographic methods to analyse hydrolysates of Merino wool derived from different strains of animals. No significant differences could be demonstrated between the analyses of wool from different sites on the same animal. Tyrosine was the only amino acid showing significant variation between strains. Simmonds (6) also investigated the amino acid composition of two Merino wools having similar diameters but different number of crimps per inch. He observed that proline was the only amino acid which showed significant differences between the two types of wool. That result contradicts the hypothesis that the amount of proline in a given wool is related to the ratio of para and ortho cortex. Syman (7), on the other hand, supporting the latter hypothesis, reports that high crimp wools contain a greater proportion of para cortex and a higher sulphur content than low crimp wools. For the sake of comparision, the amino acid analyses of fibres from different breeds of sheep and different species of animal are given in table (2.2). These results may indicate a difference between breeds and species but cannot be regarded as statistically

significant due to the non-specific nature of the analyses. The amino acid composition of human hair requires special attention as it shows the greatest variation from mean values. It is richer in cystine and proline but poorer in alanine, leucine, tyrosine, phenylalanine, glutamic and aspartic acids, lysine and arginine. This difference might be due to a high sulphur content as human hair is known to have a higher matrix content than most wool fibres. This also supports the suggestion of Dusenbury and Men Kart (8) that human hair contains only para cortical cells. Rogers and Fuilshie (9) found a higher proportion of matrix in para - than in ortho - cortical cells.

Many workers have reported the effect of the diet of the sheep on the diameter and cystine content of the wool produced. Bonsma (10) found that the sulphur content of the wool of veld sheep varied along the staple, the root sections which are produced under good grazing conditions being higher in sulphur than the middle sections which were produced during lean grazing. A sheep fed on maize showed no such differences in sulphur content. Unlike Bosma, Ross (11) found that wool grown in New Zealand during periods of high production contained less sulphur than that grown during the lean grazing period. He suggested that weathering does not alter the total sulphur content of the fibre, although some cystine is converted to cysteic acid as a result of weathering.

Due to non-uniform studies in the field there are conflicting reports by the workers. It is necessary to use controlled diets to obtain more satisfactory results in nutritional studies. For example, Maker (12) observed that by supplementingthe diet of sheep with sodium sulphate, the cystine, tyrosine, and phenylalanine contents of the wool were increased and the glutamic acid, aspartic acid, valine, leucine, and iso-leucine contents were decreased. A sulphur rich diet produced wool, longer, stronger, and greater in diameter than wool from the control group of sheep. It had been reported by Burley and Horden (13) that a copper dficient diet produced fibres containing a lower percentage of cystine. The introduction of cystine directly in the abomasum of the sheep caused a marked increase in wool production and in the sulphur content of the wool.(14)

Simmonds (15) also suggests that merino wool from a single sheep is identical at all sites of production, but there are significant differences of composition in wool samples from different sheep of the same strain.

From a structural point of view it is important to discover whether or not a protein with the composition of that in table (2.3), could exist in an α- helical form. It has been recognised for some time that certain amino acids are not compatible with the α- helix structure. In particular proline must produce considerable distortion. Lindley (15), however has pointed out that in conjunction with other residues it is

possible for proline to change the sense of the helix from right-handed to left handed. From a study of the proline and helix contents of some soluble K.M.E.F. proteins, Szent Gyorgi and Coren (16), have advanced the generalisation that

(a) three percent residues of proline randomly distributed allow 50% of the protein to form a helix, and

(b) eight percent residues of proline deforms the protein chain into a random coil. The most recent estimation of the helix content of α-keratin are about 40% by - X ray diffraction (17)

2.1 PREPARATION OF WOOL SAMPLES AND HYDROLYSIS PROCEDURE

A quantity of about 20 g of Merino, Cross (5/8+3/8 Yankasa) and pure Yankasa, Wensleydale and Balauchi wools were tipped by cutting off the top third of each lock of fibres to remove wool degraded by weathering. The root wool was extracted 40 times with diethyl ether, cleaned and then 40 times with absolute alcohol in the soxhlet apparatus. The extracted wool was cleaned ~~by hands~~ and then washed with distilled water (8 times) The clean wool was dried by the centrifuge and then finally pressed in between filter papers. Adhering vegetable matter (burr) was removed by combing the locks through fingers. The locks were drawn out by hand into slivers gilled into one long sliver and chopped into pieces. Finally the wool was stirred with distilled water and the water was decanted.

The washing procedure was repeated eight times and the wool was dried. The sample was stored in stoppered bottles in the dark.

Before use, a bottle was unstoppered and the wool was conditioned for a week in a humidity of 65-67% (in the atmosphere of saturated solution of ammonium nitrate).

Every time a sample was taken for the analysis, a similar sample was removed for moisture content determination.

2.2 PREPARATION OF HYDROLYSATE

In preparation for the amino acid analysis, samples of wools (0.25g) were accurately weighed and then hydrolysed for 18 hours in HCl (10 Cm^3, 5.7 N HCl) under reflux. To calculate the dry weight of the wool, similar samples were weighed and dried to constant weight at 105°C to determine moisture contents. After refluxing, the acidic solution was filtered to remove the humin produced during hydrolysis and then HCl was removed in vacuum using a rotary evaporator which operated in conjunction with a water bath held at 35°C. The residue (after removal of HCl) was treated thrice with distilled water which was removed by rotary evaporator. Finally the residue was dissolved in 25 Cm^3 water of which 0.1 Cm^3 was used for analysis.

2.3 AMINO ACID ANALYSIS

Samples of hydrolysates ($0.1 cm.^3$) with the addition of 0.2 μ moles norleucine, were run on the TECHNICON MODEL NCI Amino Acid Analyser, using hydrazine ninhydrin reagent. The flow diagram of the Technicon Analyser is given on page 35.

The amino acids were separated by gradient elutions on an ion-exchange column. The eluted amino acids were treated with ninhydrin solution and the colour produced was measure at 570 μm. Proline is an exception, the coloured complex of this amino acid with nin-hydrine was at 440 μm. Norleucine was used as an internal standard and the determination of colour yield of the other amino acids relative to nor-leucine enabled quantitiative analysis to be carried out.

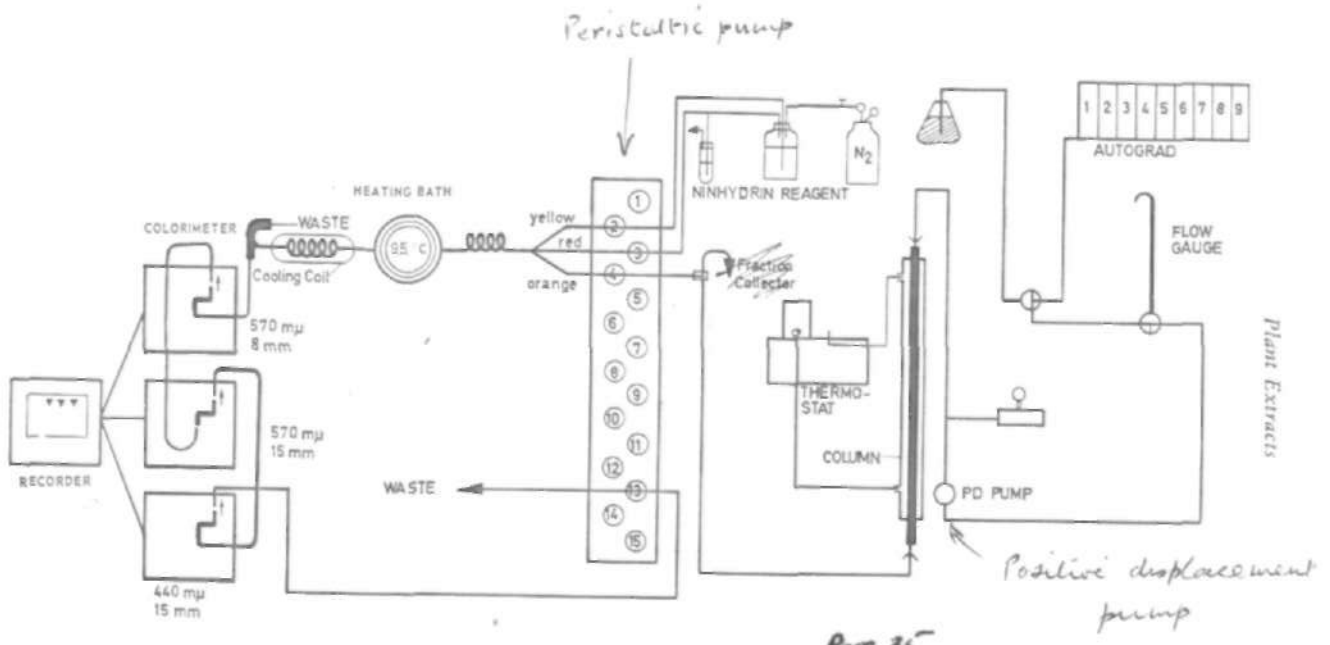


Figure 10 Flow Diagram — Amino Acid Analyzer (see Page 35)

Sample weights

(corrected for moisture, but not for ash content)

No.	1	0.394 mg
	2	0.439
	3	0.437
	4.	0.441
	5	0.412

$$\frac{\mu\text{moles amino acid}}{} = \frac{\text{Area of amino acid peak}}{\text{Area of norleucine peak}} \times \text{colour factor} \times 0.2$$

(0.2 is number of μmoles of internal norleucine standard)

Colour factors

(Hydrazine - ninhydrin reagent)

Asp	1.048
Thr.	1.022
Ser.	0.989
Glu.	1.019
Pro.	2.40
Gly.	1.138
Ala.	1.091
Val.	1.003
CyS_2	1.598
Met	1.111
Ile.	1.008
Leu.	1.014
Tyr.	1.011
Phe.	1.033
Lys	0.889
His.	0.880
Arg.	0.942

Table No. 2.1.

Amino Acid Compositions of Animal Fibres Derived from Various Strains or Breeds of Sheep and Other Species (19)

Amino acid	Merino 70's[a]		Merino 64's[a]		Corriedale 56's[a]		Lincoln[b]		Mohair[a]		Human hair[a]	
	1d	IIe	I	II	I	II	I	II	I	II	I	II
Alanine	3.51	415	3.51	417	4.37	524	4.16	493	3.80	452	2.93	345
Ammonia	7.92	937	7.46	887	9.27	1112	7.89	936	6.68	793	6.76	797
Arginine	19.35	575	20.32	602	18.21	546	20.00	592	16.52	490	16.15	476
Aspartic acid	4.68	555	4.24	503	4.86	584	4.96	588	4.58	544	3.52	415
Half-cystine	6.50	768	7.93	943	6.80	817	7.18	852	6.81	808	12.07	1422
Glutamic acid	8.54	1011	8.58	1020	9.69	1160	8.79	1040	8.89	1055	7.58	885
Glycine	6.60	781	5.80	688	6.40	769	4.80	568	5.43	645	4.34	512
Histidine	1.48	59	1.46	58	1.59	63	1.65	65	1.76	70	1.58	62
Isoleucine	2.13	252	1.97	234	2.38	286	2.48	294	2.29	272	1.80	212
Leucine	5.37	635	4.90	583	5.51	659	5.93	703	5.66	672	3.94	464
Lysine	3.19	189	3.25	193	3.72	224	4.46	264	3.75	223	3.02	178
Methionine	0.37	44	0.31	37	0.37	44	0.37	44	–	–	–	–
Phenylalanine	2.28	270	1.75	208	2.35	284	1.88	234	2.06	245	1.21	143
Proline	5.12	605	5.33	633	5.52	662	4.50	533	4.68	557	6.39	753
Serine	8.63	1020	7.25	860	7.71	925	6.33	750	6.28	745	7.22	851
Threonine	4.12	487	4.61	547	4.84	582	4.23	501	4.06	482	4.58	542
Tryptophan	1.38	163	1.73	205	1.80	214	–	–	–	–	–	–
Tyrosine	3.09	366	2.97	353	3.11	373	2.00	237	1.64	194	1.07	126
Valine	3.56	422	3.57	423	4.50	540	4.29	508	5.59	663	4.16	490
Nitrogen (%)	16.57		16.62		16.80		16.58		16.60		16.50	

TABLE. 2.2 AMINO ACID COMPOSITION

Sample No.	MERINO		CROSS		YANKASA		WENSLEYDALE		BALAUCHI	
	µmol/g	Res/1000	µmol/g	Res/1000	µmol/g	Res/1000	µmol/g	Res/1000	µmol/g	Res/1000
Asp	566	64	555	69	545	67	625	71	535	66
Thr	602	68	538	67	483	60	593	67	535	66
Ser	1014	115	910	113	860	106	1018	115	920	113
Glu	944	109	870	108	1180	146	1085	123	994	122
Pro	663	75	500	62	529	65	594	67	520	64
Gly	678	76	710	88	580	71	594	67	672	83
Ala	479	54	454	56	447	55	515	58	486	60
Val	530	60	426	53	421	52	476	54	430	53
$Cy S_2$	989	111	820	102	725	89	885	100	840	103
Met	30	3	33	4	41	5	40	5	32	4
Ile	264	30	214	27	288	35	284	32	267	33
Leu	640	72	613	76	655	81	679	77	691	85
Tyr	315	36	303	38	217	27	238	27	250	31
Phe	212	24	219	27	199	25	199	23	224	28
Lys	253	28	240	30	291	36	264	30	365	33
His	61	7	59	7	59	7	48	5	53	7
Arg	625	71	570	71	597	74	695	78	612	75

Table. 2.2 AMINO ACID COMPOSITION.

Table 2 . 3

AMINO ACID ANALYSES: WOOL BY VARIOUS AUTHORS. (MERINO 64's)

N as % Total N of wool

Amino acid	Present work	Simmonds	Corfield etal.	Graham etal.,
Asp.	5.66	4.24	4.38	4.7
Thr.	6.02	4.61	5.12	4.8
Ser.	10.12	7.25	8.66	-
Glu.	9.44	8.58	8.48	9.2
Prol.	6.63	5.33	5.05	6.1
Gly.	6.78	5.80	6.29	-
Ala.	4.79	3.51	4.12	-
Val.	5.30	3.57	4.16	4.2
CyS_2	9.89	7.93	7.30	9.9
Met.	0.30	0.39	0.32	0.4
Ile.	2.64	1.97	2.44	3.0
Leu.	6.40	4.90	5.85	5.3
Tyr.	3.15	2.97	2.62	2.7
Phe.	2.12	1.75	2.12	2.1
Lys.	5.06	3.25	3.92	3.9
His.	1.22	1.46	1.91	1.8
Arg.	18.75	20.3	19.1	21.1
Typ.		1.73	0.82	-

2.4 DISCUSSION

The main difference between results obtained in the present investigation and those obtained by Bradbary et.al., and Corfield etc. may be accounted for the more severe hydrolysis conditions employed in the preparation of the samples. It is well known, for instance, that the release of valine and isoleucine from peptides is slow, while serine undergoes decompositions during hydrolysis(18).

Therefore, variations in the amino acid analysis of similar samples are to be expected. Furthermore, the results of any investigation are accurate to not less than 5% when the auto-analysis is used.

The comparision of three wools, Merino, Cross, and Yankasa (Local) is given on page (37). The calculations and results of amino acid analysis by different authors are given on page (36) on subsequent pages for the sake comparision. Table (2.1) gives the percentage of nitrogen from total nitrogen of the wool.

Table (2.3) gives the amino acid composition of animal fibres derived from various strains of sheep and species (19).

2.5 Table.2.4 COMPARISION OF AMINO ACID

Asp.	Merino	>	Cross	>	Local (Yanksa)
Thr.	Merino	>	Cross	>	Local "
Ser.	Merino	>	Cross	>	Local "
Glur.	Merino	>	Cross	<	Local "
Pro.	Merino	>	Cross	<	Local "
Gly.	Merino	<	Cross	>	Local "
Ala.	Merino	<	Cross	>	Local "
Val.	Merino	>	Cross	>	Local "
Cysr.	Merino	>	Cross	>	Local "
Met.	Merino	<	Cross	<	Local "
Ile	Merino	>	Cross	<	Local "
Leu	Merino	>	Cross	<	Local "
Tyr.	Merino	>	Cross	>	Local "
Phe.	Merino	<	Cross	>	Local "
Lys	Merino	>	Cross	<	Local "
His	Merino	>	Cross	=	Local "
Arg.	Merino	>	Cross	<	Local "

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WORK TO STRETCH

3.1. INTRODUCTION.

During the past five decades, a considerable amount of work on th relationship between the mechanical, physical and chemical properties of wool has been carried out primarily on the basis of the fundamental concepts put forth by Speakman as early as 1926 (1,2).

Due to the very complex and heterogeneous nature of the structure of wool, and the incomplete knowledge of the interactions of proteins. the exact nature of the relationship between these properties is still not fully understood. However, such studies have been fruitful in helping to explain details of fibre structure and in providing information of considerable practical importance in wool research and industry.

The well-known stress-strain characteristics of wool fibres, which become evident under suitable conditions, are deduced from load-extension curves . which demonstrate three distinct phases:

(i) an initial region from zero to about 2 percent which obeys Hook's Law;

(ii) a yield region, in which a small increase in the stress results in a large increase in strain, ranging from 2 to 30 percent, followed by

(iii) a post-yield region, up to 70 percent, in which the increasing stress required to produce a given increase in strain is greater than in the yield region and where resistance to extension decreases just before the fibre

~~the fibre~~ breaks.

Shorter (3) showed that perfect elasticity of the fibre was invariably maintained when wool fibres were stretched even as much as 70 percent, in either air or in cold water, and then released in cold water. However, upon subsequent application of load, the resistance to extension was reduced to a degree dependent on the initial extension and the time taken to achieve it, thus indicating some form of irreversible damage (4).

However, when extension not exceeding 30 percent was carried out rapidly, in water at room temperature, the load-extension curve was reproduceable, if the fibres was relaxed for several hours in water, indicating that permanent damage was negligible (5).

Such reversibility led to the development of a sensitive 'mechano-chemical' method for studying changes in fibres subject to chemical and physical treatment (6).

The extension of single fibres under load had been studied by Harison (7), Karger and Schmidt (8), Shorter (9), Astbury and Woods (10), and especially by Speakman (11,12,13), whose work has become the basis of several methods extensively used in modern wool research to reveal changes, following the treatment of wool with particular reagents.

The fibre shows a considerable amount of elastic hysteresis and YW0 represents the curve obtained during unloading at a constant rate after the fibre has been stretched to 20 percent extension (~~Fig. 2~~).

The load extension curve up to 20 percent extension obtained when the fibre is immersed in water at 22°C provides us with a calibration for the fibre. The effect of a chemical treatment on the extensibility and reversibility can thus be assessed in terms of relative work necessary to stretch fibre 20 percent extension before and after extension.

So far, it has not been possible to explain fully the form of the load-extension curve from either experimental or theoretical treatments. The early work of Astbury and Woods (10) dealing with the analysis of x-ray diffraction patterns of animal fibres before and after stretching, setting and super-contraction, attributed the stress-strain characteristic to an unfolding of chains in non-crystalline and crystalline regions. It was proposed that to extend a whole fibre to 25 percent affected only the 'intermicellar' and 'non-crystalline' regions; the cell wall would extend up to 50 to 60 percent in a swelling agent; and the micellar region would produce a final extension of 100 percent under several conditions. The model assumed an easy unfolding of 'non-crystalline' regions of the fibre, the shoulder of the load-extension curve occurring when chains in the crystalline regions, which has greater resistance to deformation, are unfolded. The model was based on the observation that when a fibre was stretched, the characteristic α -pattern decreased in intensity with a simultaneous appearance of a β -pattern, similar to that produced by unstretched silk, which increased in sharpness

and intensity as strain, temperature, and time under stress increased. Virtually, no β-pattern was observed until the fibre had been stretched at least 20 percent. However, it was later shown by Bendit (11,12) that the α-pattern begins to disappear, and the β-pattern spacings begin to appear, when the fibre is extended as little as 5 percent, the intensity of the α-pattern decreasing smoothly and continuously and the β-pattern increasing until the fibre breaks.

In view of these findings, confirmed by Skertchly and Woods (13), and the present state of knowledge of the fine structure of the wool fibre, revised models for explaining the stress-strain characteristics have been proposed.

Skertchly and Woods proposed that the equatorial scatter of x-rays by wool fibres, after various extensions up to 60 percent in water, are the result of a continuous transformation from crystalline α-keratin to crystalline β-keratin. They further proposed that there exists an intermediate state (β'') in which the keratin is not sufficiently well-ordered to contribute to certain equatorial peaks. It has been explained that the differences in the three states are due to differences in lateral cross-linking, in parallel, between the transformable units. The loosely cross-linked units transform independently, and the closely cross-linked units transforms/this fraction being in either the crystalline α-or together β-state.

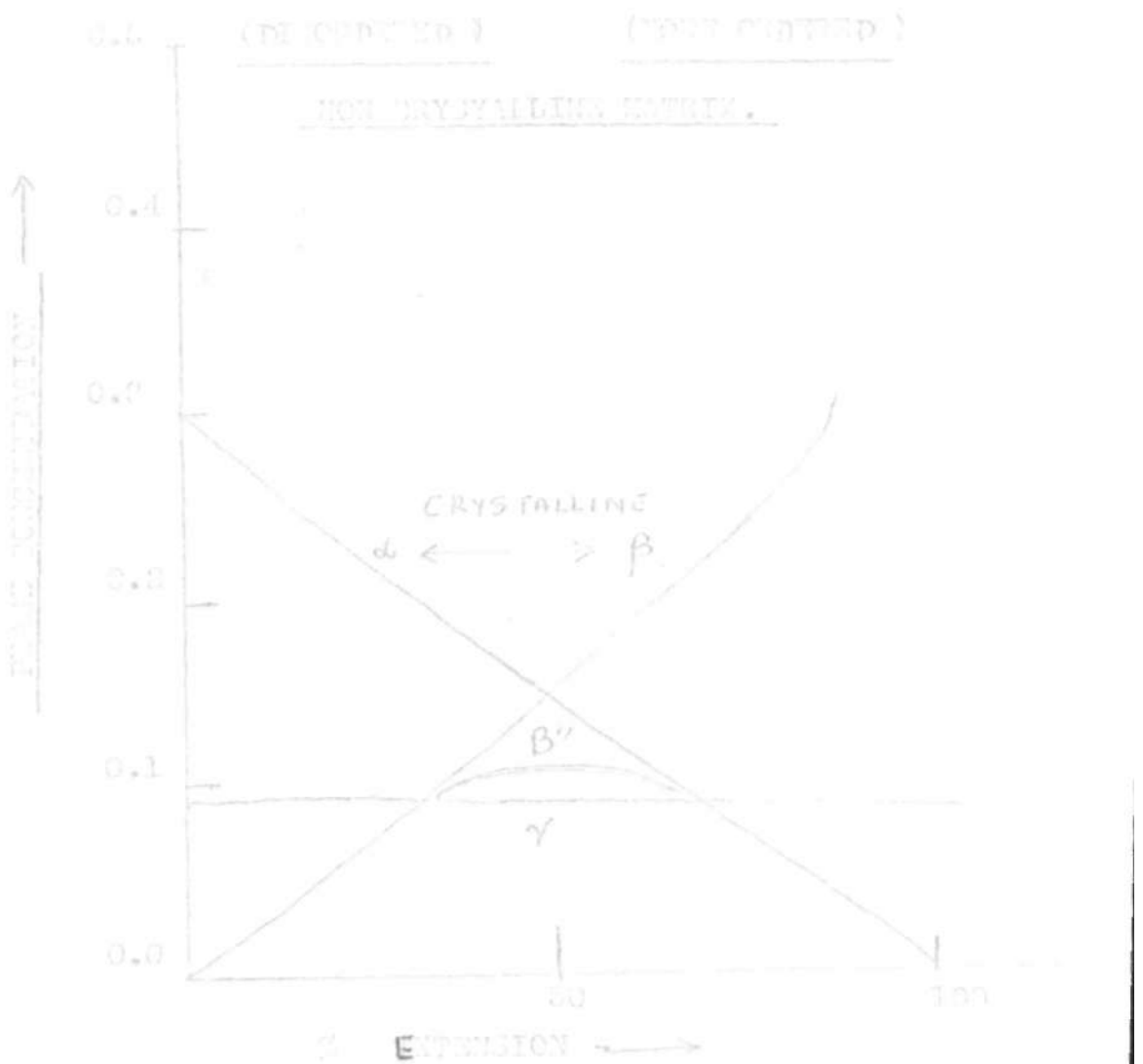


FIG. 12 , RELATIVE CONCENTRATION OF PHASES IN COOL RESULTS AT DIFFERENT EXTENSION. THE α- AND β PHASES ARE CRYSTALLINE, β'' IS A LESS CRYSTALLINE, γ AN INTERMEDIATE PHASE. THE α PHASE ARISES SLOWLY WITH EXTENSION. Ref (13)

Hence, at low and high extensions, where the majority of units are units of either α-or β-, the probability of an extended region being 'crystalline' is high, while at intermediate extensions, when α- and β- are present in comparable numbers, the probability of combination over an extended region to give a 'crystalline' structure is much lower.

Skertchly (12) has proposed that the microfibrils transform between the crystalline α- and β-phases, while the matrix, an initially disordered 'non-crystalline' phase, tends to assume a state of greater order. It means the matrix acts independently and in parallel. The residual stress at high extensions (post-yield region) is attributed to deformation of the matrix. Cross-linking between the microfibril and the matrix is not considered to take place as it would disturb the coninuous α - β-transformation.

Bendit (17a), however, was not able to reconcile the idea of a molecular α - β-transformation with the lack of inter-connection between the intensity changes of the characteristic equatorial reflections. Rather, he believes that the α-crystalline phase first goes into a more random configuration when the assembly of α -helices are distorted by stretching. The 'crystalline' phase changes and 'melts' and a cross-linked 'liquid' phase develops, indistinguishable from the non-crystalline material present in the cortex. Further, at high extensions, these two regions would contribute to the total β-materials produced.

FIG. 12.

TWO PHASE MODEL FOR WOOL STRUCTURE (a) AXIALLY ORIENTED MICROFIBRILS, C EMBEDDED IN A LOW-MODULUS (MATRIX M-(b) PARALLEL ARRANGEMENT OF THE C AND M'-PHASES) (Ref. 15)

C = Microfibrils (low modulus)
M = Matrix.

Hence, under certain conditions of temperature, humidity, etc. it is possible to envisage the disruption of α-material without its transformation into β-material which will be formed from the initially 'non-crystalline' material. The concept of a 'melt' phase makes the α - β-transformation a random event, a proposition rejected by Skertchly and Woods (14).

In recent years, the work of Feughelman has been an enormous stimulus to interest in mechanical models for wool. Originally, a two phase model was proposed (15). The crystalline microfibrils were conceived to have a high modulus (compared to matrix) and to provide the major extensional stability of the fibre. On the other hand, they were not expected to contribute much to the torsional modulus which would depend more heavily on the soft matrix. When dry, the modulii of these two components were taken to be the same, since hydrogen bonding would stabilize both. This model agrees roughly with the observed morphology and gives qualitatively the right explanations for several experimental observations. When the fibre is extended in water, the X-zones (lightly cross-linked) in the matrix allow the microfibrils (aligned helices), (Figure 12) - alongside to be extended with little opposition. X-zones open when the fibre is extended into the yield region. The Y-zones (heavily cross-linked) in the matrix oppose extension and are responsible for the increase of stress opposing extension of the fibre in the post yield region. The stress increase is time dependent and is considered to be due to the presence

of very viscous' material in the γ-zones, due to the assumed high density of disulphide groups and entanglement.

An alternative approach favoured by Feughelman (16) regards the microfibrils as having alternating χ and γ zones in series, the $\alpha - \beta$ helices of which differ in mechanical stability. During the yield-region extension of the fibre in water, the low - stability x zones open up under constant stress.

A model proposed by Munakata (20) based on microfibrils of the order of 60A^{o} width composed of Pauling and Corey AB6 cables has little relevance since the microfibril is of the order of 75A and there is no evidence for an AB6 cable in keratin.

Furthermore, the model of Crewther and Dowling (21) suggests that microfibrils consist mainly of α-helics linked to each other and to the matrix by disulphide, and acid - labile covalent bonds. The matrix is considered to consist of globular ' protein molecules with an ordered structure stabilized by intra - chain disulphide bonds and linked to similar molecules or to the microfibrils by a few inter-chain disulphide bonds and hydrogen bonds. The matrix is considered to exhibit 'plastic' flow rather than elastic properties and its viscosity is believed to be determined by the rate of thiol - disulphide interchange when stressed, and by a number of intra-molecular hydrogen bonds. The resistance of wool to protease attack, despite the large amounts of water absorbed by the matrix may be explained by this model.

The concept of a non-contractile matrix, in the Crewther and Dewling model, can be criticised, on the basis of electron microscope and x-ray studies of supercontracted fibres. No apparent twisting of fibrillar elements was observed in cortical material (19, 23) and the x-ray diffraction pattern showed marked disorientation of α or β structures in the fibres attributed to the contraction of the matrix. Further, the Crewther and Dowling model appears to neglect the known fine structure of α-keratin since the contractile microfibrils are considered as an array of parallel α-helices. Feughelman (24) revised his view about the origin of the X- and Y-zones. The two regions of differing mechanical stability were considered to exist in the matrix alongside the crystalline microfibrils.

The X-zones, on extension, allow the adjacent connection between the X and Y zones in the matrix. The X-zones were considered to be the regions of slight cross-linking and the Y-zones of heavy cross-linking. This model helps in explaining the behaviour of wool on extension after supercontraction and swelling.

Contrary to the Feughelman hypothesis, another model was presented by E. Menefee (25) which helps in elucidating the mechanical properties of wool. Menefee suggests that the fibre contains two axially parallel parts (a) a microfibril made up largely of low stability α-helices and (b) matrix consisting of arrangements of high stability α-keratin chains and amorphous protein partly extended in an axial direction. In his model, the matrix has a modulus considerably higher

than that of the microfibrils. On extension, β-keratin may originate from both the α-chains and the amorphous chains. Due to the high modulus attributed to the matrix, the fibre structure appears to correspond mechanically to a honeycomb, at least with respect to the tensile properties. In compression, the microfibrils exhibit a high modulus, so that the composite structure also has some features of pre-stressed concrete with the microfibrils assuming the role of the high compression - modulus cement and the matrix that of high tensile modulus cable.

This model fails to explain the formation of extended matrix which is obtained during extension.

EXPERIMENTAL

3.2.1

Three qualities of wool, Nigerian Merino 64, cross ($\frac{5}{8}$ Merino + $\frac{3}{8}$ Yankasa and pure Yankasa wools were used. The wool tips and roots were cut, followed by successive extraction in ether and absolute alcohol, each extraction providing 40 syphonings at the soxhlet reservoir. After extraction, the dirt and grease were removed by hand and the wool finally washed eight times in a large quantity of distilled water to remove alcohol. The purified and clean wool was dried with filter paper and kept in a desiccator containing a saturated aqueous solution of ammonium nitrate to give a relative humidity of 65% as near to 23°C as possible. In nearly two weeks time the fibres attained equilibrium.

3.2.2 METHODS

The selected fibre was mounted on a cardboard frame with sellotape and kept again inside the desiccator for a week for conditioning. A gauge length of 2cm was used and a rate of elongation and recovery at 100%/minute throughout the experiment. The fibre was then immersed in the desired solution for the selected time throughout at room temperature and constant room RH. (65% ± I) maintaining some slack in the fibre so as not to inhibit swelling.

In order to study the effect of temperature upon elastic properties, the fibres were kept (a) in ice at 0°C (b) in water at 22°C (c) in hot water at 90°C. The effect of humidity was studied by extending dry fibre kept in absolutely dry glycerol for four days at room temperature. It was extended further at RH. 65% and in water (liquid water) to maintain 100% RH (approximately.).

The fibre was then extended 20% based upon the gauge length in the swollen condition at a rate of 100%/minute. The cross head was reversed immediately and brought back to the initial position at a speed of 2 in/min.

In order to obtain the load-extension curve of single fibre immersed in a liquid, a special adapter was constructed for the INSTRON. (vide Page 54) The adapter permitted straining the fibre while completely surrounded by the liquid in the polythene beaker. The solutions of zinc chloride (M/3), cobalt chloride (M/3), manganese chloride (M/3) and nickel chloride (M/3) were filled turn by turn in the polythene beaker and the fibres were extended inside these solutions.

Two other temperature, 0°C and 90°C besides room temperature (22°C) were used. In case of zero temperature the polythene beaker was filled with ice cold water with thermometer inserted in it to record and maintain the temperature constant. After the experiment, the cold water was removed through the tap fixed at the bottom of the beaker and boiling water was add and the experiment was repeated at 90°C.

In another set of experiments the fibre was extended at room temperature in air in a constant humidity room.

To study breaking point, the fibre was extended in air with a constant rate of loading. At the point of break, the Instron's pen traced a horizontal line and came to a position of rest. From the chart, the stress at the breaking point was read. The time for breaking and the percentage extension were also calculated at the breaking time (vide Table 3·8)

Chemicals.

All the reagents and chemicals, used were of A.R. quality throughout. The solutions were made in CO_2 free distilled water and the concentrations are expressed either percent (w/v) or in molarity.

3.2.3 THE INSTRON TENSILE TESTING INSTRUMENT

The Instron is a Textile tester which uses the bonded-wire type of strain gauge. A general view of the table model is seen in Figure (←)

In order to accomodate a wide variety of specimens, several interchangeable load cells containing the strain gauges are used. In this way a range from 2 to 100,000 g is possible. The load cell is located centrally in the fixed crosshead. The upper jaw is suspended from the cell through a universal coupling. The lower jaw is mounted on the traversing crosshead which is driven upwards and downwards by screwed rods on each side.

A range of gear changes enables the speed of cross head, i.e. the rate of extension of the specimen, to be varied in steps from 0.02 to 50in/min. on the bottom panel of the crosshead assembly the controls which governs the movement of the crosshead can be seen.

The load cell output is fed by cable to the control cabinet which houses the various electronic circuits and the pen recording equipment. The main controls for load range selection, calibration, etc., are mounted on the front panel below the recording chart.

The load weighing system: The load cell consists of a grid of very fine wire bonded to the surface of the beam. Four strain gauges are used and are connected in the form of a Wheatstone bridge, each gauge having a nominal resistance of 120 . The block/circuit diagram, vide Page 54 ~~Figure~~ 4 shows a simplified picture of the method of converting the unbalancing of the bridge into a record of the behaviour of the specimen under load.

The Wheatstone bridge net work of strain gauge in the load cell is excited from an oscillator at a frequency of $375_c/s$. The amplitude of this oscillator is stabilised at a constant value by a separate circuit. An applied load on the cell changes the resistance balance of the bridge and the resulting signal is amplified by a circuit which also includes means of initially balancing the bridge.

The gain of the amplifier can be varied in steps by a load selector switch, and a calibration control can also vary the sensitivity continuously between any of these steps. A zero button shorts out

the input to the following amplifier so that the zero position of the recorder may be adjusted without the presence of any load cell signals.

The signal is further amplified and then rectified by a circuit which includes the zero adjustment of the recorder.

From this last circuit the output is a dc. signal which is fed to the potentiometer type of recorder, where it is compared electrically with the voltage across a balancing slide wire. Any unbalance between the two voltages converted by a vibrator into a 60 c/s a.c. signal and amplified to operate the pen driver motor, which simultaneously moves the pen and also the slidewire shaft until the recorder is again in balance.

Hence, the effect of extending the specimen is to cause the pen to move across the chart a distance proportional to the tensile force in the specimen. By moving the chart simultaneously a load-elongation curve is traced.

The instron is a versatile instrument which even in standard form can be used for many types of test.

Load-Extension

3.3.0 Discussion

The discussion is divided into five sections.

3.3.1 Work to stretch to 20% extension

(a) Effect of time inside water

The work to stretch 20% falls slowly with time as the fibre is kept inside the water.

Vide graph ..curve.20,21.On.page.83.....

It will be seen, that in general the fibre may be stretched readily and to a greater extent as the moisture content of the wool is increased.(27) There is opening of more hydrogen bonds as time passes. The recovery work also falls with time where the phenomena of setting and super contraction is more predominant. (30,31,32).

(b) Effect of temperature in Water

The work to stretch Merino wool up to 20% ~~increases~~ decreases as the temperature of water increases from zero °C to 90°C.

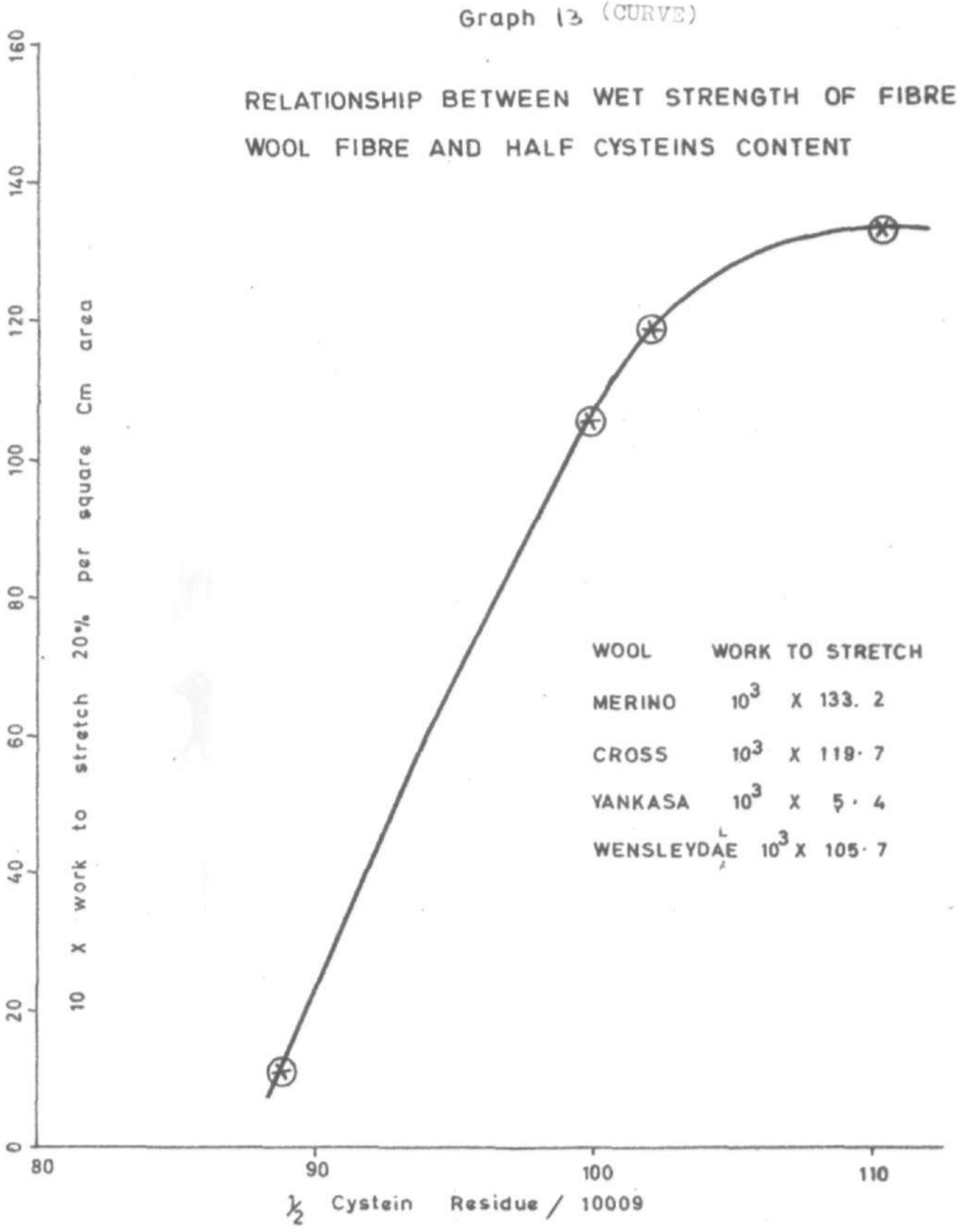
The results are as under:

$0°C > 22° > 90°C$

$46.8\ g\,den^{-1} \times 10^{-2} > 42.9 > 25.35\ g\,den^{-1} \times 10^{-2}$

Limiting stress of Hooke's law region is also found to decrease continuously as the extensibility increases, the shoulder of the curve becoming less definite. The sharpness and intensity of the β-pattern increases with strain, temperature and with time. (26,27,28,29).

Graph 13 (CURVE)



Hence increasing the temperature has a similar effect as that of humidity on the shape of the load-extension curve, and makes the fibre easier to stretch. At elevated temperature, stressed disulphide bonds are essentially easier to break. These disulphide bonds are reformed in equilibrium with the extended state. On release, there is a lower tendency for the fibre to return to its original state.(6)

(c) Effect of humidity

The work to stretch 20% for a dry fibre was as high as 1.05 $g den^{-1}$ and decreased with the increase of humidity.

It is generally accepted that the fibre (27) may be stretched more readily and to a greater extent as the moisture content of wool is increased.(2) As the water content of the fibre increases from absolute dryness to saturation, the entire curve is inclined towards extension and the load at Hookean stress is reduced to its lowest value. In a dry fibre, the effect of disulphide bond rupture is either very small or not apparent. In wet fibres, the microfibrils bear most of the breaking stress, whereas at lower relative humidity, the matrix bears a significant part of the breaking stress.

(d) Effect of H Cl (0.2M) at 22°C

The work to stretch 20% of the fibre gradually decreases with time until it reaches 0.189 $g\ den^{-1}$ after 24 hours.

There is one point to note, that the work to stretch the fibre inside water and inside H Cl for five minutes are very close (0.872 and 0.785). It is evident that the complete opening of hydrogen bonds and the unfolding of disulphide bonds are not possible within five minutes. Nevertheless, as time passes, there is a vast difference in their values.

Table.3.1 Work to stretch: g den^{-1} x 10^{-2} (MERINO)

Time	Water	H Cl.
5	78.5	87.0
10	42.9	42.0
60	-	32.0
180	25.00	-
1440	23.8	18.9

A possible explanation of these effects is that the variable nature of bonds breaking due to difference in penetration along the fibre. Breakdown of salt links, a relatively slow process may be contributory to this.

If a mechanical model for the fibre is assumed, where the mechanical behaviour in the yield region is produced by the microfibrils, while the behaviour in the post yield region is due to a combination of microfibrils and some other component (matrix?) then the similar absolute decreases in

the stress values in both regions would indicate that the mechanical effect of bond breakdown is restricted to the breaking produced in the microfibrils. Because of the rapid changes from the yield region to the post yield region found for both water and H Cl, the behaviour appears to fit best the Feughelman zone model (15), where sudden structural changes are predicted for the post yield region.

(e) Thioglycollic acid.

The effect of thioglycollic acid seems to be very mild as there is not much difference in the value of work to stretch the fibre in water and in the acid (vide Table 3.4) Due to the short time treatment (10 minutes) and at temperature 22°C, the reagent is not effective.

The reaction with TGA requires many hours to reach the equilibrium state. The extent of reaction is markedly affected by the concentration of TGA in solution (82).

(f) Formic acid

The behaviour of formic acid (50%) is not altogether different to that of hydrochloric acid or water. The significant difference is the work index which is 75% (HCl = 63%, water = 47%).

It has already been pointed out that Merino wool behaves differently in diameter swelling. According to the recent finding by Bendit (12) there is still a significant

fraction of the α-helix present even in 100% formic acid. Pure formic acid (100%) releases all the hydrogen bonds so that the initial Hookean region is either totally eliminated or progressively diminished. Beyond 2 percent extension the helices become pulled out into the β-form gradually. This begins to show up positively through X-ray photography at 20% extension which reveals the formation of β-keratin. The same explanation has been forwarded by Szucht (85).

(g) Formamide

The work to stretch 20% in formamide is very high. This might be due to less structural changes inside the fibre. The opening of hydrogen bonds is obvious but the breaking of disulphide bonds is not effective. Most probably, the formamide treatment is mild.

(h) Alcohols (Ethanol and Iso-propanol)

Early findings by Speakman showed that wool fibres stretched in water, methanol, ethanol or n - propanol showed increasing work to stretch 30% in that order. In n- butanol or n - amyl alcohol the fibre behaved like anhydrous wool. There was a progressive decrease in the amounts of the various alcohols absorbed by the fibres to a minimum of 0.3% with n - amyl alcohol. Speakman suggested that the larger molecules could not penetrate the fine structure of the fibre. The high degree of iodination of tryosine residue

of wool in ethanol, and incomplete iodination in n-propanol was explained in the same way by Richards and Speakman (38).

However, Bradbury and Leador (71) have shown that with prolonged equilibrium in anyhydrous alcohols, wool fibres absorb essentially equal volumes of water, methanol, ethanol, n - propanol, isol-propanol, and n - butanol amounting to 34.1 cm^3./100g.

They suggested that the 'pores' in wool vary in size owing to thermal fluctuations and swelling. They also demonstrated considerable volume of contraction when water was absorbed by wool. The data of work to stretch 20% extension for ethanol and n-propanol is very close. It seems to indicate the same order of penetration and the same amount of absorption. The pore size theory on which basis the absorption of any solvent depends is now totally rejected.

(i) Phenol

Alexander (41) observed that the stress at which the Hookean region ends is greatly decreased by immersing the fibre in aqueous phenol. He also reported that when a fibre is stressed in dilute aqueous phenol it swelled considerably and become much weaker. He further obsérved that the effect was fully reversible and on stretching the fibre in water alone it could regain its original strength.

As usual, there is breaking of hydrogen bonds when the fibre is stretched in aqueous phenol. The possibility of breaking of disulphide bonds cannot be ruled out. There is a possibility of the occurrence of super contraction as it was reported by Elod and Zahn (42)

The few hydrogen bonds which are not broken by water are possibly broken by phenol. When the fibre is stretched in dilute aqueous phenol, it swells making the fibre weaker. The rate of breaking of hydrogen bonds depends upon the diffusion of OH-ions; and as time passess, more hydrogen bonds have been servered. The reduction of Hookean stress (3.0g) supports this view.

TABLE NO. 3.2 LOAD EXTENSION

AIRING

TEMPERATURE 22 C. EXTENSION 20% (Constant)

TREATMENT	CONCENTRATION	TIME FOR TREATMENT MINS.	Work to stretch g. don^{-1} x 10^{-2}	Work Recovery g.don^{-1} x 10^{-2}	Work Index %	Hookean Stress (g)	Hookean Stress per initial area g x cm^{-2} x 10^{6}
$ZnCl_2$	M/3	10	38.2	15.5	47.0	7.4	2.94
		1440	35.1	14.0	40.0	4.1	1.61
		2880	17.8	9.2	48.0	4.3	1.69
		4320	16.1	8.5	53.0	3.49	1.49
$CoCl_2$	M/3	10	38.0	17.5	46	8.0	3.15
		1440	32.7	20.7	63		
		2880	26.6	14.6	55	4.2	1.65
		4320	21.0	10.4	52	5.4	2.13
$NiCl_2$	M/3	10	51.3	26.9	51	27.0	10.7
		1440	50.0	25.0	50	26.0	10.2
		2880	29.4	14.2	48	9.4	3.86
		4320	22.1	11.2	51	8.3	3.53
$MnCl_2$	M/3	10	49.4	29.4	59	55.0	1.97
		1440	43.0	29.4	63	10.6	4.2
		2880	39.0	20.0	51	6.0	2.4
		4320	18.5	11.1	60	6.8	2.8

TABLE NO. 3.3 LOAD EXTENSION

MERINO AND CROSS WOOLS

TEMPERATURE 22°C. EXTENSION 20% (Constant)

		CROSS					
TREATMENT	CONCENTRATION	TIME FOR TREATMENT MINS.	WORK TO STRETCH $g.den^{-1} \times 10^{-2}$	WORK RECOVERY $g.\ den^{-1} \times 10^{-2}$	WORK INDEX %	HOOKEAN'S STRESS (g)	HOOKEAN STRESS PER INITIAL AREA $g \times cm^{-2} \times 10^{+6}$
$ZnCl_2$	M/3	10	29.2	17.3	59	11.8	4.08
		1440	26.6	12.9	48	7.6	2.63
		2880	18.0	7.6	42	3.8	1.32
		4320	12.3	6.8	55		
$CoCl_2$	M/3	10	37.1	19.1	51	4.8	1.66
		1440	28.4	15.8	55	16.7	5.77
		2880	20.0	12.0	60		
		4320	12.0	6.0	50	1.9	0.66
$NiCl_2$	M/3	10	45.1	21.8	48	16.4	5.67
		1440	45.0	21.4	47	16.2	5.60
		2880	23.0	11.7	50	4.8	1.66
		4320	12.7	5.7	45	3.7	1.30
$MnCl_2$	M/3	10	58.5	32.0	55		
		1440	58.0	28.1	48	12.5	4.32
		2880	52.9	25.4	48	13.0	5.65
		4320	51.1	25.0	49	22.8	7.78

TABLE NO. 3.4 LOAD EXTENSION

MERINO AND CROSS WOOLS

TEMPERATURE 22°C EXTENSION 20% (Constant)

TREATMENT	CONCENTRATION	MERINO: TIME FOR TREATMENT MINS	MERINO: WORK TO STRETCH g.den^{-1} x 10^{-2}	MERINO: Work Recovery g.den^{-1} x 10^{-2}	MERINO: % Work Index	MERINO: Hookean Stress (g)	MERINO: Hookean Stress per initial area g x cm^{-2} x 10^{6}	CROSS: WORK TO STRETCH g.den^{-1} x 10^{-2}	CROSS: Work Recovery g.den^{-1} x 10^{-2}	CROSS: % Work Index	CROSS: Hookean Stress (g)	CROSS: Hookean Stress per initial area g.x cm^{-2} x 10^{6}
Water	~~1%~~	5	78.5	35.8	46	-						
		10	42.9	20.3	47	-		45.0	26.8	59.6	-	
		180	25.0	12.5	50	-						
		1440	23.8	12.4	52	-		31.5	18.2	57.8		
		2880						28.6	14.5	50.7		
		4320	17.8	11.1	60	16.4		22.6	13.4	59.3		
HCl	.2M	5	87.2	65.1	75	15.0	5.9	25.4	15.7	62.0	4.9	1.79
		30	40.2	25.3	63	8.0	3.15	25.4	15.7	62.0	4.9	1.79
		660	32.0	18.0	57	4.0	1.58					
		1440	18.9	10.9	58	2.5	.99					
Formic acid	50%	5.0	46.4	34.7	75	9.8	3.85	22.9	14.0	61.0	3.1	1.16
		10.0	42.2	24.3	57	4.4	1.73	20.7	10.4	50.0	2.8	1.07
Acetic Acid	5%	5	25.7	15.1	59	4.6	1.80	29.3	13.7	47.0	3.3	1.27
Thioglycollic acid		10	47.9	23.3	49	3.8	1.49	16.7	7.2	43	2.1	0.81
Absolute alcohol	99%	5	68.9	42.2	61.3	11.6	4.56	2.0				
		10	52.9	29.1	55.0	9.0	3.54	16.2	8.8	56	3.2	1.23

TABLE NO. 3.5 LOAD EXTENSION

MERINO AND CROSS WOOLS

TEMPERATURE 22°C CONSTANT EXTENSION = 20%

		MERINO						CROSS				
TREATMENT	CONCENTRATION	TIME FOR TREATMENT MINS.	WORK TO STRETCH g.den^{-1} x 10^{-2}	Work to Recovery g.den^{-1} x 10^{-2}	Work Index (%)	HOOKEAN STRESS (g)	Hookean Stress per initial area g. cm^{-2} x 10^{6}	WORK TO STRETCH g. den^{-1} . 10^{-2}	Work Recovery g. den^{-1} . 10^{-2}	WORK INDEX (%)	HOOKEAN STRESS (G)	HOOKEAN STRESS PER INITIAL AREA g. cm^{-2} x 10^{6}
Isopropyl Alcohol	99%	10	50.7	26.9	53	10.2	4.01					
Phenol	10%	30	55	35.4	64	12.8	5.03					
		60	51.0	32.9	64	8.9	3.5					
		120	19.7	11.9	61	3.0	1.18					
Formamide	5%	5	10.9	84.6	77	4.9	19.3					
	1	10	87.8	54.4	62	21.8	8.57	41.7	25.6	61	7.0	2.69
Dry Fibre	-	-	105.2	35.6	34	-	-	75.4	46.0	61	-	
Dry fibre	65%	-	76.8	34.1	45			37.4	14.0	38	5.9	2.26
Liquid Water			42.9	20.3	47			32.9	16.8	51	4.5	1.72
Water(0°C)			96.8	30.2	63			29.6	13.9	48	3.0	1.15
Water(22°C)			42.9	20.28	47			28.1	14.5	51		
Water([illegible])			25.9	8.2	31	3.5		24.2	10.9	45	3.6	1.38

TABLE NO.3.6 LOAD EXTENSION D/TA

YANKASA WOOL

TEMPERATURE 22°C EXTENSION 20%

TREATMENT	CONCENTRATION	YANKASA					
		WORK TO STRETCH $g.den^{-1} \cdot 10^{-2}$	WORK RECOVERY $g.den^{-1} \cdot 10^{-2}$	WORK INDEX (%)	HOOKEAN STRESS (G)	HOOKEAN STRESS $g.cm^{-2} \cdot 10^{6}$	TIME FOR TREATMENT (MINS)
~~$ZnCl_2$~~	~~M/3~~	~~4.06~~	~~2.06~~	~~52~~	~~85~~		
$ZnCl_2$	M/3	2.06	1.06	52	85.5	0.31	2880
		2.67	1.01	40			4320
$CoCl_2$	M/3	3.12	1.27	41	130	0.6	4320
$NiCl_2$	M/3	3.24	1.31	40			
$MnCl_2$	M/3	3.30	1.28	41			1440
		2,62	1.28	42			
		1.96	0.89	45			
Water		3.24	1.53	47	103		

3.3.2. BREAKING LOAD AND EXTENSION

The results of breaking loads and corresponding extension are given in the tables 1,2,3, on page (63) for three different wools.

The order of breaking load for Merino and cross is more or less the same.

For Merino it is:

HAC < formamide < phenol < water < aq. $ZnCl_2$.

formic acid < aq. HCl < aq. $MnCl_2$ < aq. $CoCl_2$ < aq. $NiCl_2$

For Cross the order is

formic acids = formamide = $ZnCl_2$ < $CoCl_2$

HCl < $MnCl_2$ < water < $NiCl_2$ - aq.

For Yankasa wool, the order is

formic acid < HCl < formamide < HAC

$NiCl_2$ < $COol_2$ < $MnCl_2$ = $ZnCl_2$ < water

From the above data it was observed that the breaking load is not the same for different wools. The Merino is the strongest as it requires more load to break. The Yankasa wool is the weakest and requires very little load to break the fibre.

When we considered the effect of different reagents upon the breaking load, we find that acetic acid, formamide and phenol are responsible for breaking disulphide bonds and unfolding of α -helix, and the fibre becomes very weak as compare to the wet fibre.

When wool is extended there is rupture of linkages and later the formation of new linkages in the extended positions:

$$R_1 - S.S. - R_2 + H_2O \rightleftharpoons R_1 - SOH + R_2SH$$

$$R_2 - SOH + H_2N-R_3 \rightleftharpoons R_2 -S-NH-R_3$$

or

$$R_2 -CH_2 - SOH \rightleftharpoons R_2 -CHO + H_2S$$

$$R_2 - CHO + H_2N - R_3 \rightleftharpoons R_2CH = N-R_3$$

If a wool has a high sulphur content the attack is preferentially on the matrix. The treatment with water decreases the breaking load more than at 65% rh or zero% rh. Elod, et. al, (42) put forward their views that the hydrolysis of relatively few peptide bonds caused a marked decrease in the breaking load of single wool fibre when the wool is treated with small quantity of dilute sulphuric acid ~~it produces chiefly aspartic acid~~. It is generally believed that the low sulphur group is derived from the microfibril and the high sulphur group from the matrix. This view was supported by the observation that the low sulphur proteins are fibrous and yield an α-pattern when oriented films or fibres were examined by X-ray diffraction, whereas the high sulphur proteins yielded only diffuse halos indicating an amorphous structure. As the low-sulphur proteins have three times the aspartic acid content of the high sulphur proteins, this suggests a preferential attack on the micro-fibrils. When wool is treated with small amount of concentrated sulphuric acid it produced chiefly serine and threonine N - terminal residues. The greater content of serine and threonine in the high-sulphur proteins suggests a preferential attack on the matrix.

Crewther and Dowling (45) observed that dilute H_2SO_4 treatment to the fibre decreased the breaking load in water than that at 50% r.h. Crewther and Dowling, further explained that in wet fibre, the micro-fibrils bore most of the breaking stress, whereas at low r.h. values, the matrix was responsible to the bear the breaking stress.

In the light of the above discussion the dry fibre must require a high breaking load. Similar effects were observed in the case of elevated temperature. It was easier to stretch the fibre at high temperature; at low temperature more load was required to break the fibre.

The order of breaking load is given as indicated in the following tables:

TABLE NO. 3.7

Breaking Load		Temperature Effect
Merino	Load/Area:	22°C < 90°C < 0°C
Cross	Load/Area:	90°C < 22°C < 0°C
Yankasa	Load/Area:	90°C < 22°C < 0°C
BREAKING LOAD		Humidity Effect
Merino:	Load/Area:water =	100% r.h. < 65%r.h < dry
Cross:	Load/Area:water =	100% r.h. < 65%r.h. < dry
Yankasa:	Load/Area:water =	100% r.h. < 65%r.h < dry

EXTENSION AT BREAKING POINT

Farrow, (46) had indicated that to extend the fibre dry, it requires more load. It is also difficult to stretch the dry fibre.

His results are given below:

Merino wool		Breaking
Tenacity:	g/tex	%extension
at 65%	14	43
(in water) at 20°C	10	57
Wet at 95°C	5	78

One striking feature which predominates throughout the investigation of elastic properties, is the behaviour of the cross wool. The % extension of cross wool at breaking point is always less than Merino and Yankasa, nevertheless one may expect its behaviour to be intermediate between the two.

TABLE 3.8 BREAKING LOAD MERINO WOOL AT TEMPERATURE 22°C

Treatment	Concn.	Time for Treat-ment.	Time to Break Secs.	Extension at Break (%)	Breaking Load (g)	Breaking Load/initial area $g/cm^{+2} \times 10^{+6}$
HCl	0.7%	15	26.5	47.5	9.5	3.7
Formic acid	95.0%	15	42.9	71.5	8.3	3.3
Acetic acid	99.0%	15	26.5	47.5	4.0	1.6
Formamide	99.%	10	34.8	58.0	5.4	2.1
$NiCl_2$	M/3	180	42.0	70.0	12.8	5.0
$MnCl_2$	M/3	180	49.5	82.5	9.8	3.9
$CoCl_2$	M/3	180	45.9	76.5	10.4	4.1
$ZnCl_2$	M/3	180	67.5	112.5	7.7	3.0
Water		180	36.6	61.0	7.2	2.8
	AT DIFFERENT TEMPERATURES					
Water (0°C)			48.5	80.8	16.2	6.2
Water (22°C)			36.6	61.0	7.2	2.8
Water (90°C)						
	AT DIFFERENT HUMIDITIES					
Dry (0% r.h.)		15	40.5	67.5	10.8	4.2
Dry (65% r.h.)			39.9	66.5	9.0	3.5
Wet (100% r.h.)			36.6	61.0	7.2	2.8
Water(100% r.h.)	4320		33.3	55.5	7.0	2.8
Phenol	30		40.5	67.5	5.1	2.1

TABLE .3.9 BREAKING LOAD: MERINO CROSS TEMPERATURE 22 C

Treatment	Conc. %	Time for treat-ment Mins.	Time to break (secs)	Extension at Break (%)	Breaking Load (g)	Breaking Load/initial area $g/cm^2 \times 10^{-6}$
HCl	0.7	5.0	42.0	70.0	6.0	2.1
Formic acid	95.0	15.0	25.5	42.5	4.6	1.0
Formamide	99.0	15.0	60.0	100.0	4.6	1.6
$NiCl_2$	M/3	180.0	38.4	64.0	7.0	2.4
$MnCl_2$	M/3	180.0	36.0	60.0	6.6	2.3
$CoCl_2$	M/3	180.0	27.0	46.5	5.5	1.9
$ZnCl_2$	M/3	180.0	77.5	46.5	4.6	1.6
Water		180.0	36.0	60.0	6.8	2.4
AT DIFFERENT TEMPERATURES						
Water (6°C)			31.1	53.5	11.3	3.9
Water (22°C)			36.0	60.0	6.8	2.4
Water (90°C)			48.3	80.5	4.0	1.4
AT DIFFERENT HUMIDITIES AND AT CONSTANT TEMPERATURE 22°C						
Dry (0% r.h.)			42.0	70.0	10.8	4.2
Dry (65% r.h.)			36.9	61.0	6.8	2.4
Wet (100% r.h.)			26.9	44.0	6.0	2.1
Water (100%r.h.)		4320 (~~Secs~~ Mins.)	33.8	56.3	4.2	1.45

TABLE NO. 3.10 BREAKING LOAD YANKASA

Treatment	Conc. %	Time for treat-ment Mins.	Time to break (secs)	Extension at Break (%)	Breaking Load (g)	Breaking Load/initial area $g/mm^2 \times 10^{+6}$
Dry at 65%			47.7	79.0	37.0	1 3
Water		180	60.0	100.0	22.5	0.8
Water (90°C)		180	44.5	82.5	22.5	0.8
$CoCl_2$	M/3	180	51.3	85.5	26.5	0.96
$CoCl_2$	M/3	180	51.0	85.0	26.5	0.96
$MnCl_2$	M/3	180	67.6	96.0	28.0	0.10
$NiCl_2$	M/3	180	53.1	88.5	25.0	0.9
$ZnCl_2$	M/3	180	60.0	100.0	28.0	0.1

TABLE NO. 3.11 BREAKING LOAD

YANKASA WOOL AT TEMPERATURE 22°C

Treatment	Conc. (%)	Time for treatment	Time to break (secs)	Extension at Break (%)	Breaking Load (g)	Breaking Load/initial area $g/cm^2 \times 10^{+6}$
HCl	0.7%		72.0	120.0	8.6	0.03
Formic acid	95%		69.0	115.0	7.2	0.03
Acetic acid	99%		61.8	103.0	14.2	0.05
Formamide	99%		52.8	87.5	10.1	0.04
		DIFFERENT TEMPERATURE				
Water(0°C)			69.0	115.0	47.5	0.17
Water(22°C)			91.5	152.5	36.5	0.13
Water(90°C)			136.5	227.5	31.0	0.11
		AT DIFFERENT HUMIDITIES AT 22°C				
Dry at 0%			52.5	87.5	51.0	0.18
Dry at 65%			64.5	107.5	47.0	0.17
Wet at 100%			67.5	112.5	37.5	0.14
Water 100%		4320 (secs)	87.0	145.0	31.2	0.11

TABLE NO. 3.12

3.3.3. STRESS AT HOOKEAN REGION FOR MERINO, CROSS AND YANKASA WOOLS AT TEMPERATURE: 22°C.

TREATMENT	TIME FOR TREATMENT in mins.	HOOKEAN STRESS/INITIAL AREA (g cm^{-2} x 10^6) MERINO	CROSS	YANKASA
$ZnCl_2$(M/3)	10	2.91	4.08	
	1440	1.61	2.63	
	2880	1.69	1.32	0.31
	4320	1.49	-	-
$CoCl_2$(M/3)	10	3.15	1.66	
	1440	-	5.77	
	2880	1.65	-	-
	4320	2.13	0.66	0.60
$NiCl_2$(M/3)	10	10.7	5.67	
	1440	10.2	5.60	
	2880	3.86	1.66	
	4320	3.53	1.30	-
$MnCl_2$(M/3)	10	1.97	-	
	1440	4.2	4.32	
	2880	2.4	3.65	0.52
	4320	2.8	7.78	0.31
HCl (0.2M)	5	5.9	1.79	
	30	3.15	1.79	
	60	1.58	-	
	1440	0.99	-	

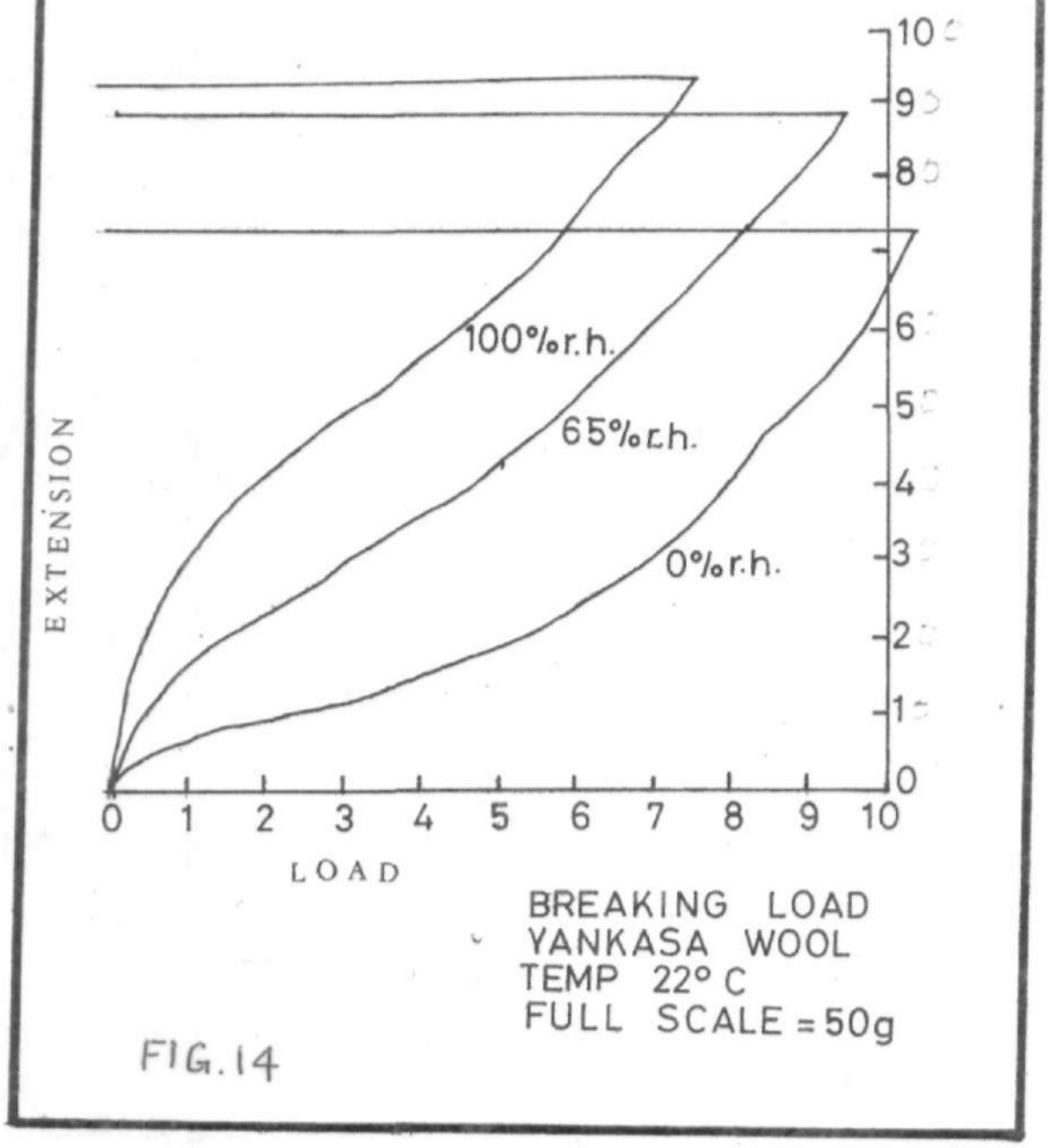

100%r.h.
65%r.h.
0%r.h.
EXTENSION
LOAD
0 1 2 3 4 5 6 7 8 9 10
BREAKING LOAD
YANKASA WOOL
TEMP 22° C
FULL SCALE = 50g

FIG. 14

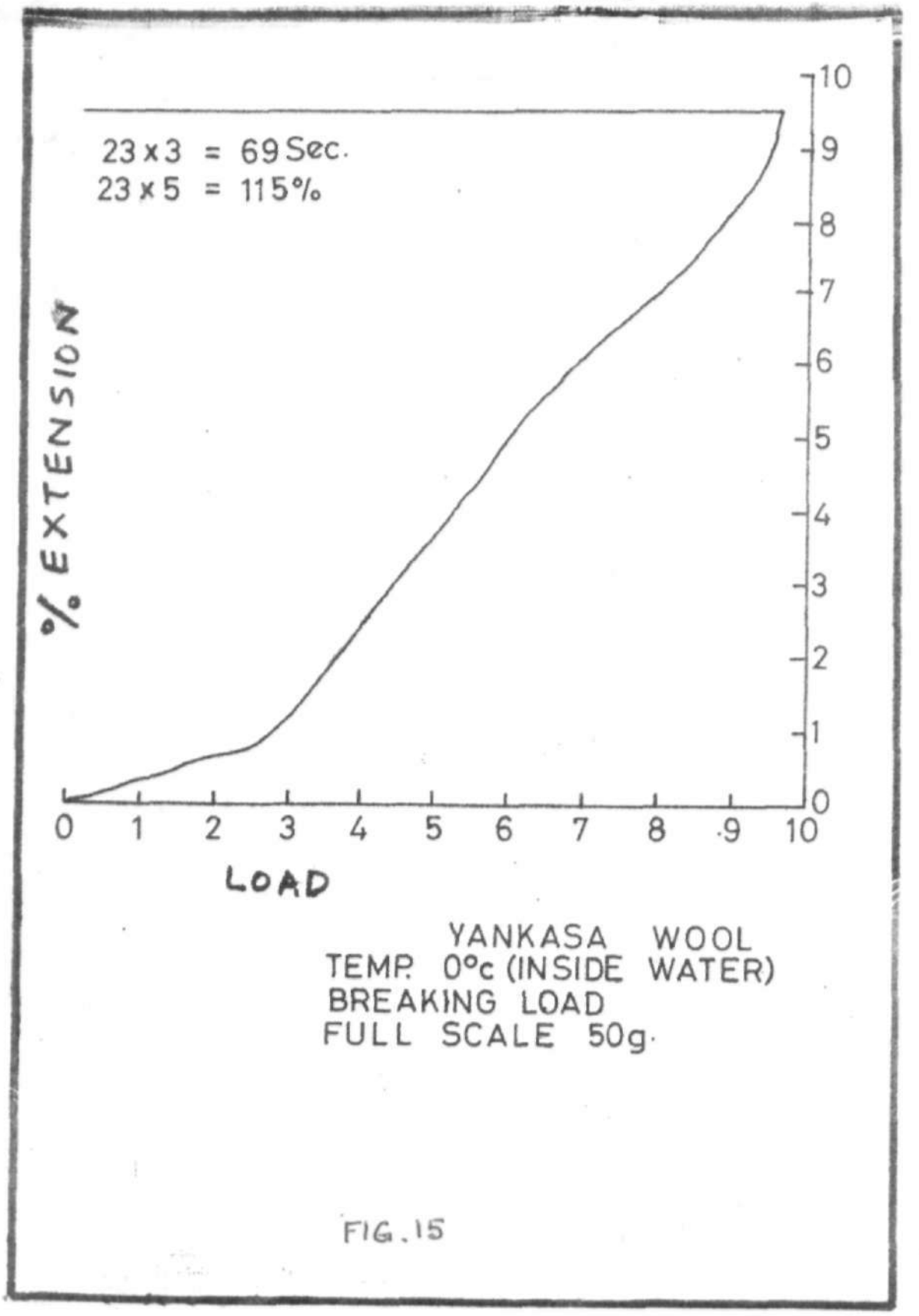

23 x 3 = 69 Sec.
23 x 5 = 115%
% EXTENSION
0 1 2 3 4 5 6 7 8 9 10
LOAD
YANKASA WOOL
TEMP. 0°c (INSIDE WATER)
BREAKING LOAD
FULL SCALE 50g.

FIG. 15

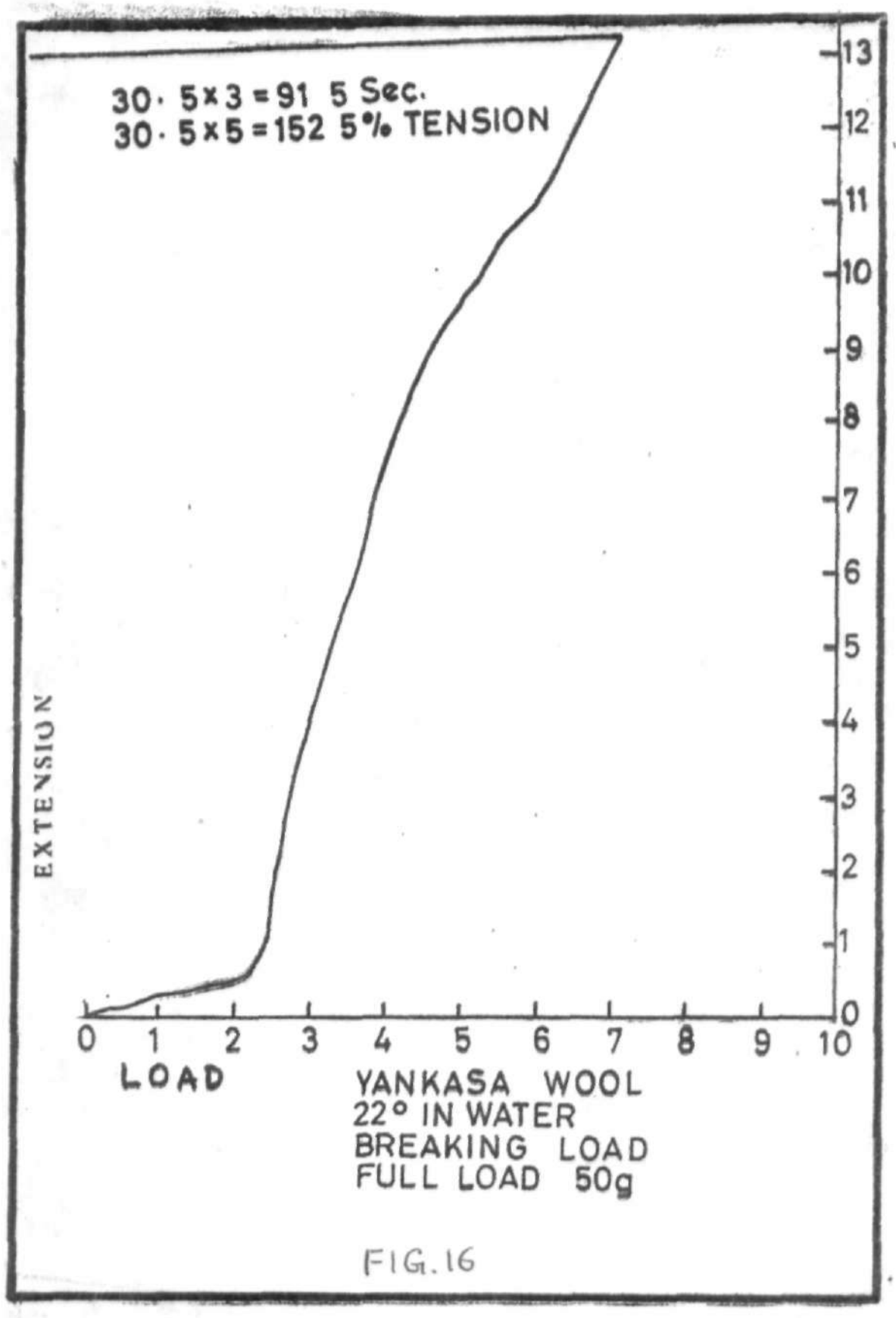

30·5×3=91 5 Sec.
30·5×5=152 5% TENSION
EXTENSION
0 1 2 3 4 5 6 7 8 9 10
LOAD
YANKASA WOOL
22° IN WATER
BREAKING LOAD
FULL LOAD 50g

FIG. 16

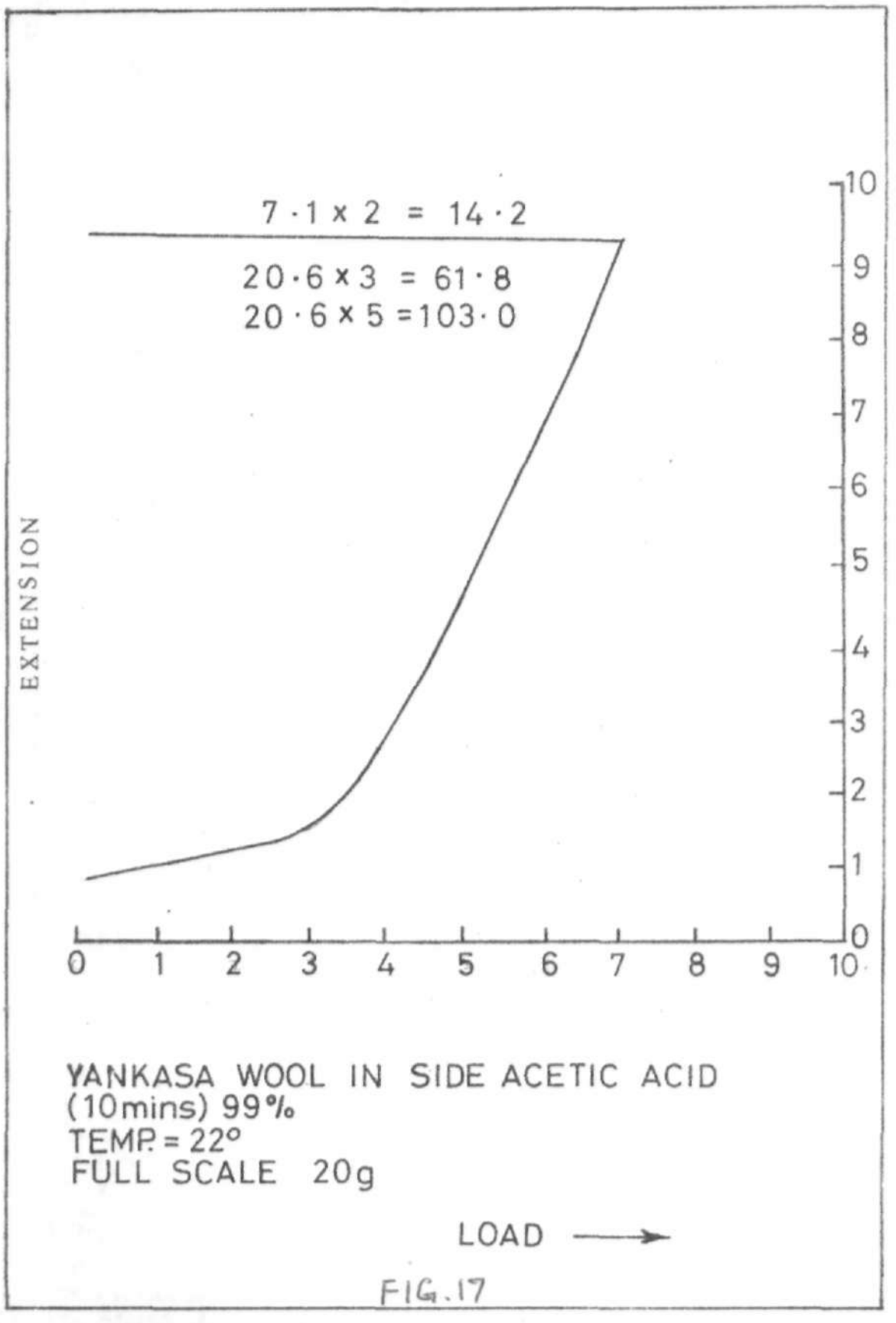

7·1 x 2 = 14·2
20·6 x 3 = 61·8
20·6 x 5 = 103·0
EXTENSION
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7 8 9 10
YANKASA WOOL IN SIDE ACETIC ACID
(10mins) 99%
TEMP. = 22°
FULL SCALE 20g
LOAD

FIG. 17

FIG. 18

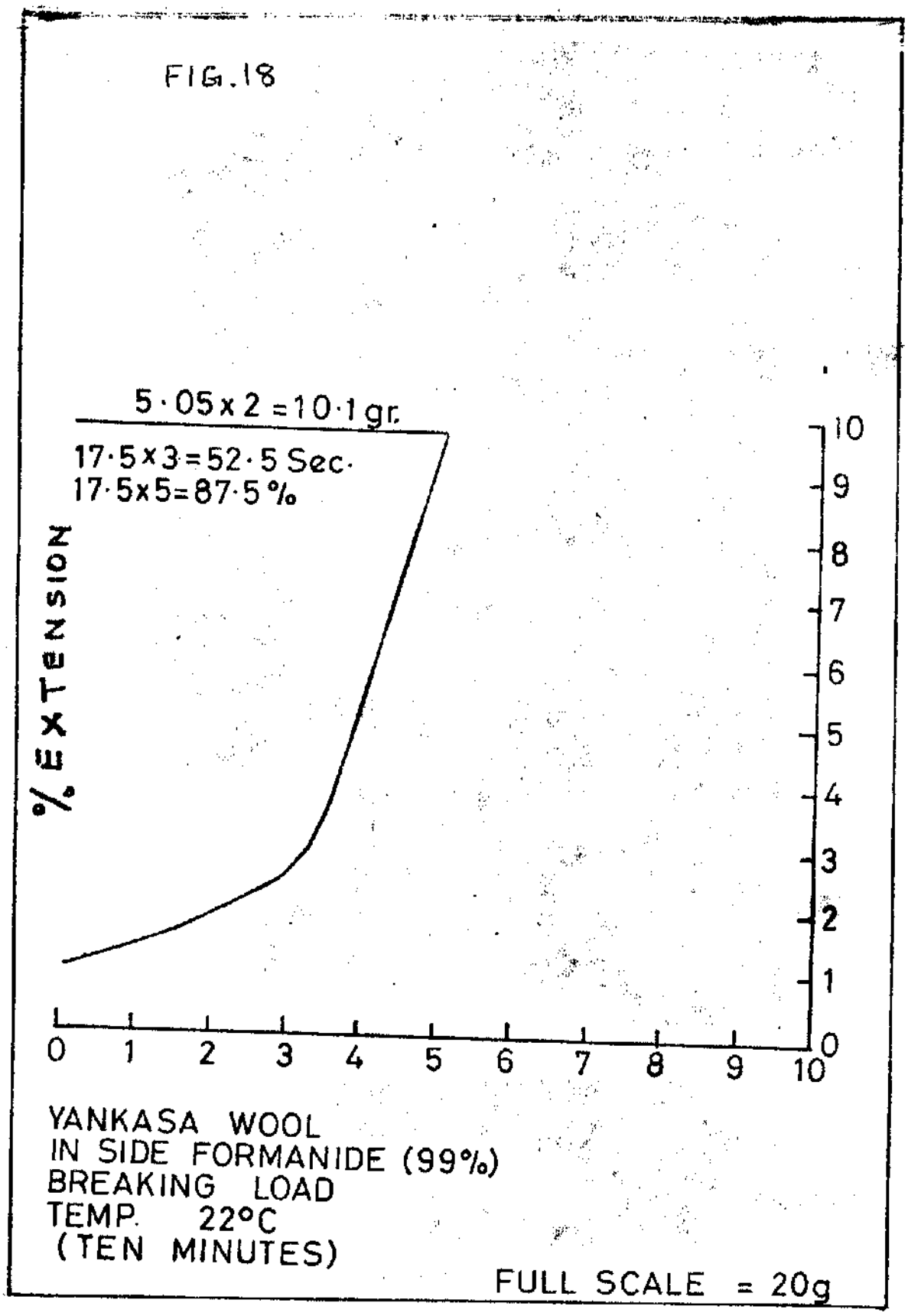
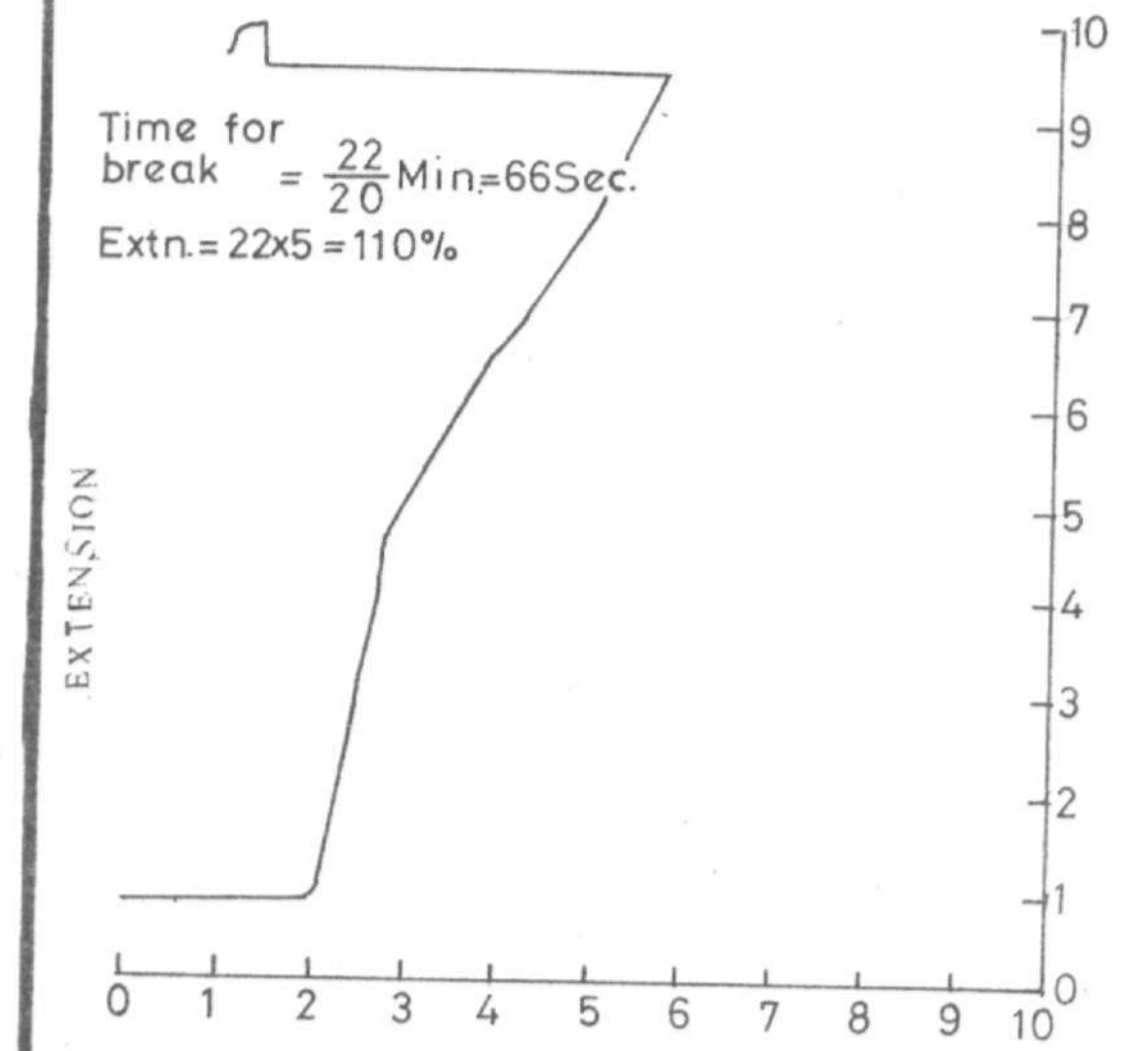

5·05 x 2 = 10·1 gr.
17·5 x 3 = 52·5 Sec.
17·5 x 5 = 87·5 %
% EXTENSION
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7 8 9 10
YANKASA WOOL
IN SIDE FORMANIDE (99%)
BREAKING LOAD
TEMP. 22°C
(TEN MINUTES)
FULL SCALE = 20g

FIG. 19



MERINO WOOL
(IN SIDE WATER)
TEMP = 90° C
FULL SCALE =10g

Table.3.13

TREATMENT	TIME FOR TREATMENT in mins.	HOOKEAN STRESS/INITIAL AREA ($g\ cm^{-2} \times 10^6$) MERINO	CROSS	YANKASA
Formic (50%) acid	5	3.85	1.16	
	10	1.73	1.07	
Acetic (5%) acid	5	1.80	1.27	
Thioglycollic acid (5%)	10	1.49	0.81	
Absolute (99%) Alcohol	5	4.56	-	
	10	3.54	1.23	
Iso-propyl (99%) alcohol	10	4.01	-	
Formamide (5%)	5	19.3	-	
	10	8.57	2.69	
PHENOL (10%)	30	5.03		
	60	3.50		
	120	1.18		
WATER ([redacted])		3.5	1.38	
WATER	4320	16.4	-	0.43

HOOKEAN STRESS

The results for Hookean stress are given in table (3.12). The stretching of a fibre within the Hookean region is considered to be stretching of chemical bonds (47, 48, 49). Alexander (47) had reported that when a fibre was stretched in dilute solution of phenol, the stress at the Hookean region is greatly reduced. Speakman (50) and Szucht (35) had observed separately that the stress at the Hookean region completely disappeared when the fibre is extended in formic acid.

Initially the fibre behaves like a spring and obeys Hooke's law which states that stress is proportional to the strain up to the yield region. This part of the curve is sometimes referred to as the Hookean region. It is noticed that when the load is removed from the fibre, it recovers its original length or very nearly so. To calculate the initial Young's Modulus, which is equal to the ratio of the stress to the strain; the ratio of the tangent of the angle to initial part of the curve and horizontal axis is obtained. A high modulus indicates inextensibility, and a low modulus, great extensibility.

Following is the data of initial Modulus of Merino wool in different solvents reported by Norman, Abbot, et al., (57)

Table. 3.14

Treatment	Concentration	initial modulus (g/tex)
air	-	360
water (22°C)	-	170
water (95°C)	-	65
Formic acid (21 C)	90%	5.4
HCl (95°C)	0.7%	64.0
Acetic acid (21°C)	90%	57
Phenol (21°C)	85%	15.0
Formamide (95°C)	50%	36.0
Formamide (100°C)	99%	1.8

From the data given in the table (3.)14 it is evident that the fibre becomes loss and less elastic as it is left in water or any other solvent except manganese chloride (M/3) solution. In the manganese chloride solution, the effect is reversed and the stress at the Hookean region increases with time. It has been noticed that either diminishing or totally eliminating the Hookean region results from the rupturing of either disulphide or secondary (Hydrogen) bonds.

Patterson et. al., (52) and Harris (53) had supported the idea that as stress was decreased progressively, the rupture of more and more disulphide bonds was (31,54) taking place.

The cross wool has lower value of Hookean stress and hence it has got greater extensibility. The Yankasa wool has got the least stress, but in some cases it is of same order as the cross wool.

3.3.4 EFFECT OF SALT SOLUTION IN PRESENCE OF ACID ON THE ELASTIC PROPERTIES OF MERINO WOOL (22°C)

TABLE NO. 3.15

Treat-ment	Vol. (cm^3)	HCl (cm^3)	Initial PH of Sol.	Time for treat ment	Work to Stre-tch	Work Recov-very	% work index	Final pH of Solv.
WATER	100	---	---	72hrs	17.9	11.3	60	----
$ZnCl_2$	100	0.0	3.9	72hrs	32.7	15.9	48	4.41
$ZnCl_2$	100	0.5	2.18	72hrs	35.1	16.9	47	3.05
$ZnCl_2$	100	1.0	2.05	72hrs	36.0	18.2	53	2.64

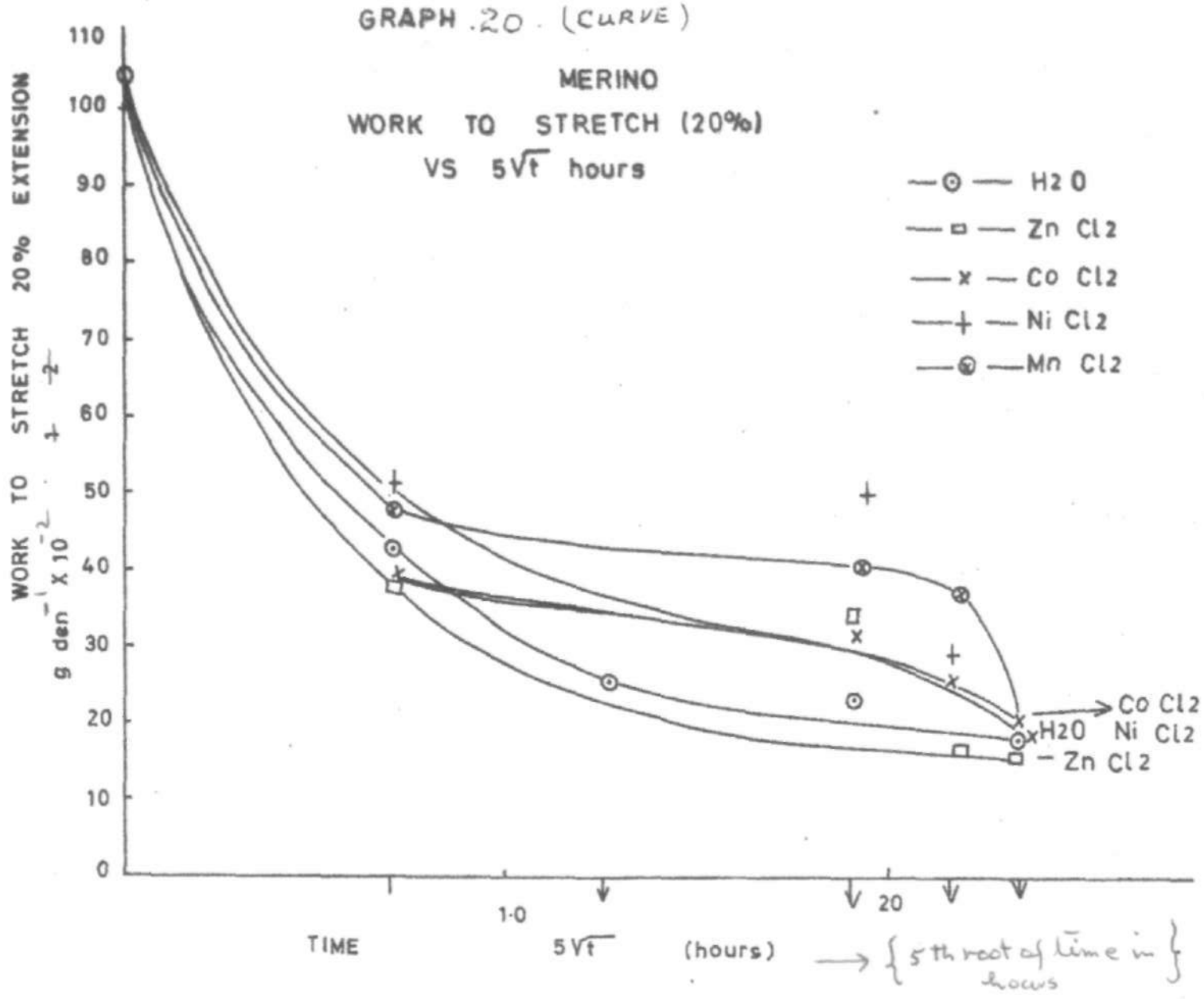
A procedure was adopted to find the effect of salt solution in presence of HCl on the elastic properties of wool (5). Four samples of Merino wools of exactly one gram each were taken. In the first sample $100cm^3$ of distilled water, in the second sample $100cm^3$ of M/3 $ZnCl_2$ solution + $0.5cm^3$ (M/1) HCl and the fourth one, $100cm^3$ $ZnCl_2$ (M/3) + $1.0cm^3$ (M/1) as indicated in Table No. (3.15). The initial pH and the final pH were obtained for the last three samples. The final pH was measured after three days.

Assuming that equilibrium had been established after 72 hours, one single fibre from each sample was mounted on the cardboard square keeping a 2cm. gauge length. The fibres were then extended to 20% extention. The work to stretch, work recovery, and percentage work index were calculated from the results (Table 3.15).

It was stated by Sookne and Harris (55) andBogoty, Sookne and Harris (56) that the reduction in work required to extend the fibre by 30% in N/10 HCl solution saturated with the KCl solution was less than in pure water. Speakman (57) considered that the comparison of reduction of work should be made with saturated KCl solution not with water alone; where it was found that the fibre were more resistant to the stretching than in the acid medium.

From the above table it is obvious that the work index in the case of water is high (60%). The value of the work to stretch in the acid medium increases as the concentration of acid increases. This supports the hypothesis that the addition of the acid makes the fibre more elastic. It is also evident from the above results that the introduction of the metallic ion (Zn^{++}) into the keratin structure makes the fibre more difficult to stretch.

GRAPH .20. (CURVE)

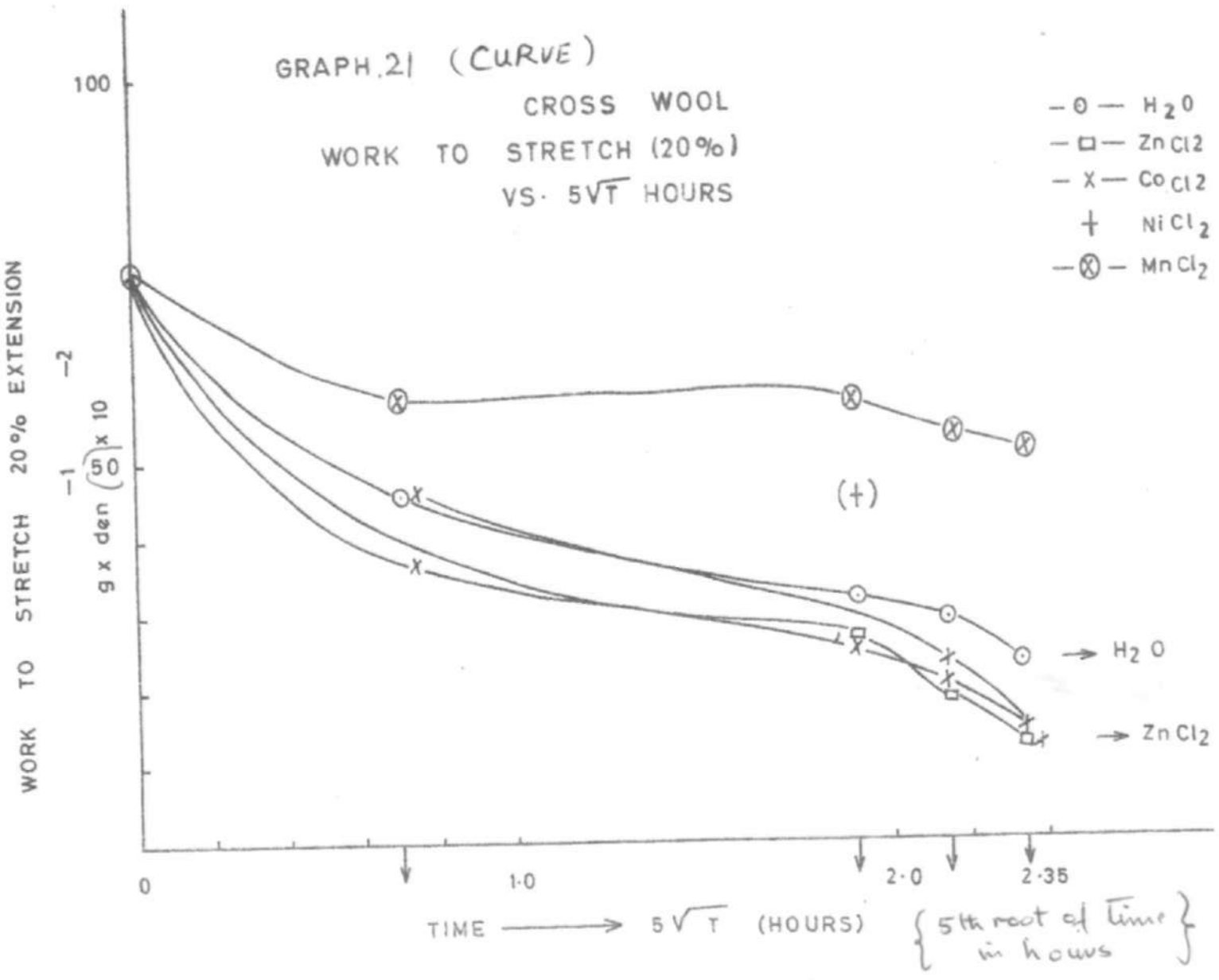


GRAPH.21 (CURVE)

CROSS WOOL

WORK TO STRETCH (20%)

VS. $5\sqrt{T}$ HOURS



3.3.5 LOAD EXTENSION AND TIME

Attempts have been made to find the relation between work to stretch 20% with time. An arbitrary equation has been established to correlate these two items. The equation is:

$$W = A - t^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where W is work to stretch, A is the work to stretch at zero time or approximately work to stretch 20% for a dry fibre at 65% r.h. and t is the time for treatment.

The equation (1) is further simplified

$$W - A = -t^{1/n} \text{ or } \log (W - A) = \frac{-1}{n} \log t.$$

On plotting the values of log (W - A) versus - log t using the data obtained from load extension experiment, the value of n may be around 18 (slope of the curve). Instead of using as 18, if n is equal to 5 (for ease of calculation), the equation becomes

$$\log (W - A) = f(\frac{1}{5} \log t)$$

This gives satisfactory equational representation of the data. The cures obtained on plotting work to stretch 20% versus $5\sqrt{t}$ where t is the time for treatment and work to stretch is w.

The complete set of data are given in the appendix.

The conclusion one can draw that the work to stretch decreases as time lapses and after certain time it reaches to approximately a constant value (vide figur 20,21.) Similarly the curves between work recovery versus time have been drawn for different types of wool in presence of water and M^{+2} ions solution for sake of comparison. (Fig. 22,23)

FIG.22.

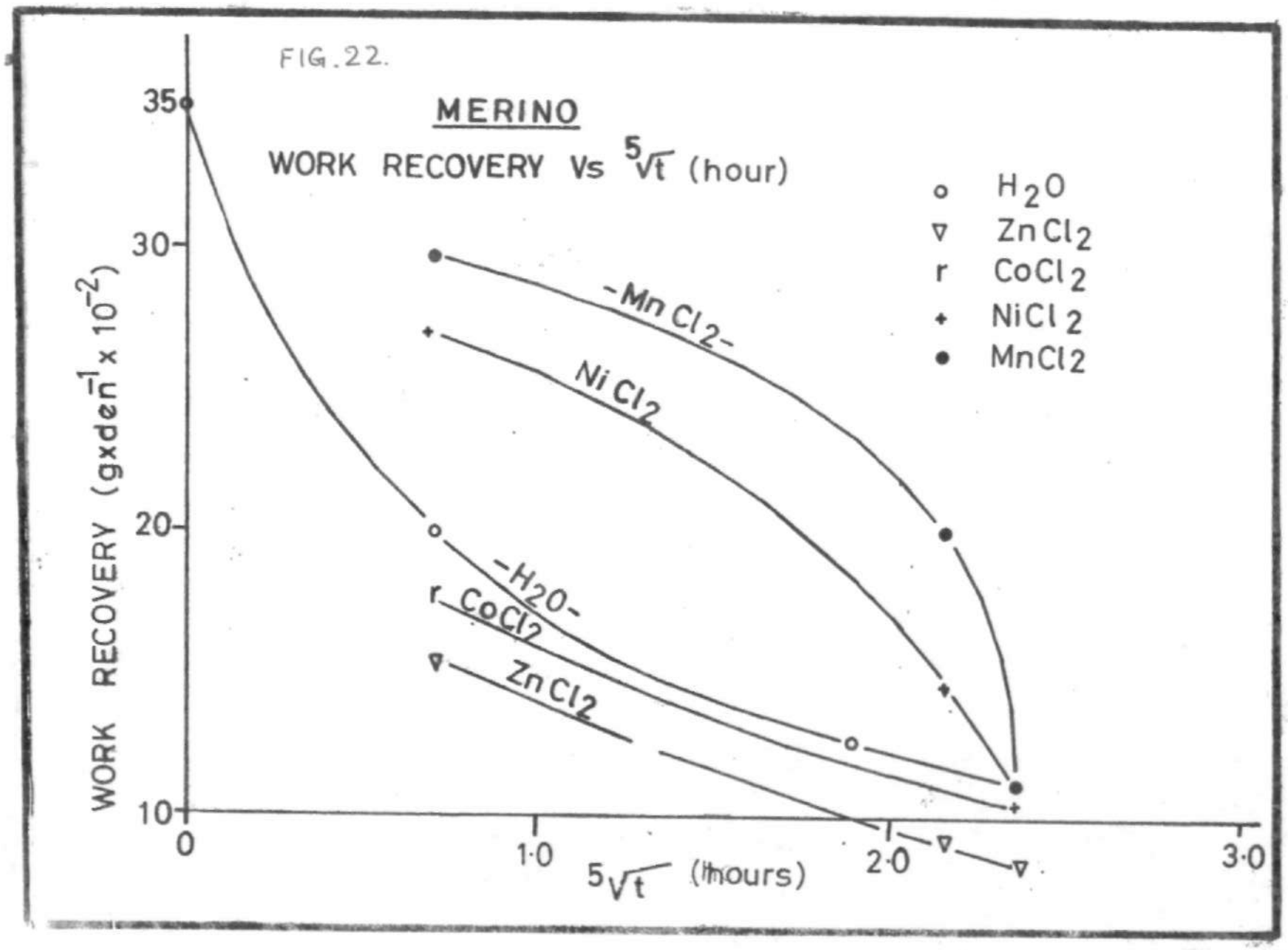
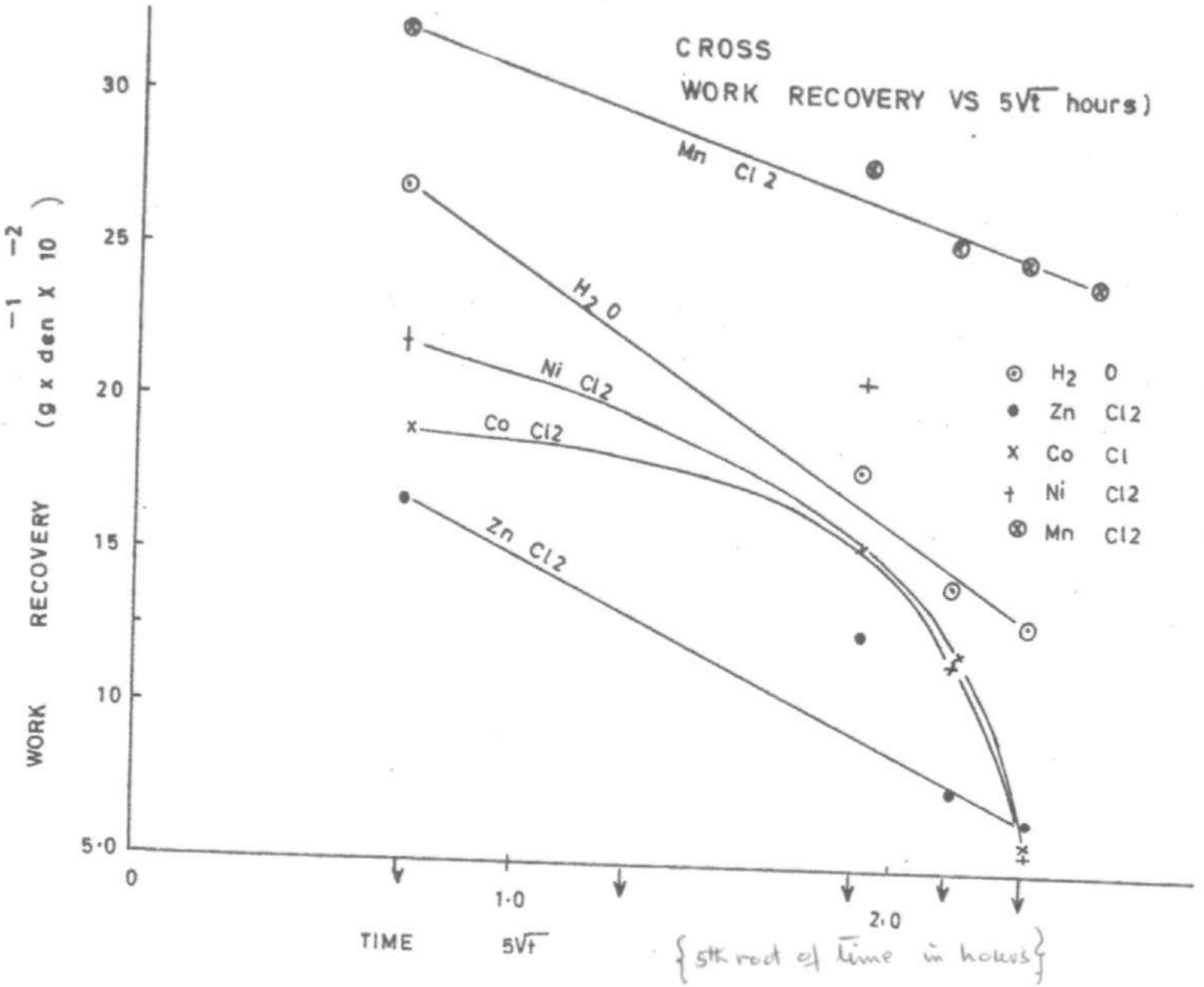

MERINO
WORK RECOVERY Vs $\sqrt[5]{t}$ (hour)
o H_2O
▽ $ZnCl_2$
r $CoCl_2$
• $NiCl_2$
● $MnCl_2$
-$MnCl_2$-
$NiCl_2$
-H_2O-
r $CoCl_2$
$ZnCl_2$
WORK RECOVERY (gxden^{-1} x 10^{-2})
35
30
20
10
0
1·0
2·0
3·0
$5\sqrt{t}$ (hours)

FIG. 23


CROSS
WORK RECOVERY VS 5√t hours)
WORK RECOVERY (g x den X 10 -1 -2)
30
25
20
15
10
5·0
0
1·0
2·0
TIME 5√t
{5th root of time in hours}
Mn Cl 2
H2 0
Ni Cl2
Co Cl2
Zn Cl2
⊙ H2 0
• Zn Cl2
x Co Cl
† Ni Cl2
⊗ Mn Cl2

3.3.7 SUMMARY OF THE RESULTS

Load Extension at Breaking point.

WOOL	Less than water	Greater than Water	Remarks
LOAD			
Merino	HAC, formamide	$ZnCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$ HAC, HCl	Cross in intermediate (i) Those greater than may act by dehydrating of the fibre. (ii) Those less than water may be due to swelling and H-bond breaking (iii) Yankasa is : 20 times weaker, Cross wool 14th time weaker than Merino
Cross	formamide, $ZnCl_2$, $CoCl_2$, HAC, $MnCl_2$	$NiCl_2$	
Yankasa	all	none	
EXTENSION			
Merino	HAC-HCl, formamide	$NiCl_2$, $CoCl_2$ $MnCl_2$, formic acid, $ZnCl_2$	
Cross	HAC, $CoCl_2$, $ZnCl_2$	$MnCl_2$, $NiCl_2$, HCl, formamide	
Yankasa	all	none.	

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SWELLING

4.1 INTRODUCTION.

One of the most important properties of wool is its hygroscopic nature, that is, its capacity to absorb water vapour from a moist atmosphere or to lose it to a dry one. The term regain is used to express water content in the wool fibre. It is defined as the weight of absorbed water expressed as a percentage of the dry weight of the wool, in other words, it is the weight of water which a perfectly dried sample would have to regain to recover its original condition.

The equilibrium regain of the wool is considerably affected by its previous treatment, although its absorption properties can always be restored by soaking in water at room temperature except when chemical action has taken place. One natural consequence of regain changes in wool fibres is the corresponding change in fibre volume. This, on account of the highly anisotropic nature of the wool fibre, is shown largely as an increase in fibre diameter, the length of the fibre remaining almost unchanged.

The first complete study of the swelling of wool in moist atmospheres was made by King (1). Speakman also calculated radial swelling on the assumption that there is little longitudinal swelling (2). Hirst tried to find the swelling in different liquids (3). Further measurements of the radial swelling of wool were made later by Warburton using a cored fibre method. The resistance of such a pipe to a flow of air depends both on the diameter of the core, and on its eccentricity. With a wool fibre as a core, the eccentricity is not accurately known, but since it does not change as the fibre swells the variation in cross-section can be obtained with reasonable accuracy (4).

The swelling of wool (1-10) in different liquids has been previously explored, but the aims were directed to other objectives. In this work, the purpose of determining the swelling of wool in different liquids was to answer the following questions satisfactorily and to lend support to the model of wool proposed. As well as, comparing the 3 different wools studied, the questions to be answered are:

(i) whether the effect of large adsorbed molecules are due to increasing cohesion between adjacent peptide chains, i.e. a a direct physical effect of absorbed material;

(ii) is there any exchange of solvent with water, or totally exclusion of water;

(iii) is there any cross-linking or any breaking of bonds;

(iv) whether any physical or chemical effects occur such as electrostriction; and

(v) is there any inhibition of thio-disulphide interchange, either by changing the "internal PH" or by direct oxidative or blocking effect.

There were variations in swelling data, but in most of the cases the variation was not more than ten percent at constant temperature. The variation may be due to different types of fibre from same quality of wool. There was another difficulty during the measurement of swelling, to measure the diameter accurately because, diameter varies along the length of the fibre. To avoid this discrepancy the diameter was always measured at particular place. In addition, the cross-section of most wool fibres is elliptical and the direction of the major axis spirals down the fibre; this complicates the measurement since the fibre may possess a small amount of torsion.

4.2 EXPERIMENTAL

Direct measurements of the radial swelling of wool fibres both in moist air and in different liquids were made. Fibre diameter was measured with a microscope using a mechanical stage and a device for rotating the fibre; the measurement being made in the two directions at right angles to each other at four points along the fibre 0.1 millimeter apart. Three different Nigerian wools: Merino 64's, Cross (5/8 Merino + 3/8 Yankasa), and Yankasa were chosen. Four sets of measurement were made. The single fibre after removing the twist carefully, was taped to a microscope slide and viewed with a magnification of 600X by a microscope. Solvent was added carefully to the slide so that if flowed under the cover glass and surrounded the fibre. The diameter of the fibre was measured before addition of solvent and at various intervals of time afterward at the same point along the axis. Observations at elevated temperature were also made, but the results were not consistent for the same fibre; they were rejected.

The results were recorded as the diameter swelling and further calculations are tabulated as percentage radial swelling and percentage volume swelling. The recorded diameter is the average diameter of four

observations on same fibre. Where the increase in diameter was not uniform and the percentage swelling was beyond 5% error, these sets of reading were rejected.

It has also been noted that percentage swelling in some fibres was too high. This was noticeable in local (Yankasa) wool. These fibres after thorough checking, were found to be damaged or cut at certain places. These damaged fibres tend to absorb solvents at a much greater speed than other fibres of the same wool. The explanation which may be given to this effect is that the absorption proceeded from one fracture rather than from the surface of the fibre. In each case the cover glass was used to minimize the evaporation of liquid, though the weight of the cover glass itself might have had some effect on the swelling radially, but when the difference was noted no significant flattening was observed. To prevent shrinkage, both ends of the fibre were taped with sellotape.

The interval of time for each observation was kept uniform and swelling was observed up to 3 hours time. A limited time of three hours permitted a wide range of liquids to be studied within reasonable time period. Every attempt has been made to measure the swelling up to the equilibrium stage but the time of three hours was always kept in mind.

4.3.1 DISCUSSION

The swelling data are presented in the appendix 4 page (259), Table No.(39-41) The swelling has only been measured at constant temperature (22°C). High temperature should also be taken into consideration as high temperature effects the extent of swelling. The higher the temperature, the more the swelling by the fibre, as reported by Norman, et al, (11). Another important factor which affects the extent of swelling, is time. The observations were made at regular interval of time viz., 5, 10, 30, 60, 120, and 180 minutes.

The data reveal that the swelling in the three different wools (Merino, Cross and Yankasa) is different with respect to time. Cross wool behaves similarly to the Merino. Yankasa behaves differently. In most of the cases, the swelling of Yankasa wool is very high except in formic acid (50%), dimethyl formamide, and urea. It has been noticed that the swelling in different solvents is slightly higher in case of Cross wool than Merino wool.

The swelling of different wools is in the following order with respect to the different swelling media:

MERINO:

Formic acid 95% > phenol 90% > formaldehyde 40% > formic acid 50% > phenol 10% > hydrazine 98% > formamide 99% > urea 50% > water HCl 0.7% > dimethyl formamide 50% > acetic acid 50% > acetaldehyde 100%.

CROSS:

Formic acid 95% > formaldehyde 40% > phenol 90% > formic acid 50% > phenol 10% > hydrazine 98% > formamide 98% > urea 50% > water hydrochloric acid 0.7% > dimethyl formamide 50% > acetic acid 50% > aceteldehyde 100% > glycerol 100%

YANKASA:

Phenol 10% > phenol 90% > formaldehyde 40% > formic acid 95% > water HCl > formamide 99% > hydrazine 98% > urea 50% > dimethyl formamide 50% > acetic acid 50% > aceteldehyde 100% > glycerol 100%.

Table. 4.1

MAXIMUM SWELLING (VOLUME) OF DIFFERENT WOOLS

SOLVENT	CONCN.	VOLUME SWELLING (%)		
		MERINO	CROSS	YANKASA
Formic acid	95%	152.0	159.0	188.0
Phenol	90%	85.0	126.5	300.0
Formaldehyde	40%	82.0	128.0	224.0
Formic acid	50%	80.4	85.0	58.8
Phenol	10%	67.7	69.0	300.0
Hydrazine	98%	52.5	65.6	224.5
Urea	50%	46.4	51.7	56.7
Water	100%	36.9	34.8	104.5
HCl	0.7%	22.3	25.5	95.7
Dimethyl-formamide	50%	20.5	21.0	14.3
Acetic acid	15%	13.4	14.0	22.5
Acetaldhyde	100%	4.2	5.7	8.2
Glycerol	100%	0.0	1.0	4.7

4.3.2 SWELLING IN WATER

The maximum swelling of the different fibres in water is given on page 96 It is obvious from the data that water , easily penetrates the fibre. The absorption of water depends on the magnitude of the change in relative humidity and on the previous history of the fibe (12, 13). Shaw et, al., (14) and Haly et, al., (15) reported that at low R.H. values water is firmly bound by the wool, but as the R.H. increases from 50 to 100%, the water in the fibre becomes more mobile. Fraser et, al., (16) had pointed out, using the X-ray diffraction results, that most of the water is located in the matrix. Initially the water molecules are greatly absorbed onto certain sites and may be regarded as forming a hydrate. Later, absorption continues, by the addition of successive layers of water molecules, similar to a solid solution. Peirce (17) pointed out that the directly absorbed water had the biggest effect on the physical properties because it resulted in the breaking of cross-linkages between the molecules whereas the indirectly attached water, which in most cases easily evoporated, had greater influence on the vapour pressure.

During the absorption of water, there is evolution of heat. This effect diminishes as more water is absorbed. The heat comes from the attraction between the active groups and water or from the condensation of water vapour into a close-packed state similar to that in liquid water. It was proposed by Lynch and Marsden (18) that the absorbed water existed as small clusters of no more than a few molecules even near saturation absorption.

Absorption by the wool has been divided into three stages (27); water first becomes attached to the groups in the side-chains and then to groups on the main chain and finally it is indirectly attached. The firmness with which the first water molecules are fitted into the wool molecules explains the very slight change in such properties as torsional rigidity and dielectric constant up to regains of 8%. It is noted that at higher regains these physical properties show a marked change. Initially a greater number of bonds are ruptured in a very short time. When allowed to remain in the solution for a longer time, say 120 minutes, fibres which acquire a fair degree of set, manifest a small decrease in the value of longitudinal

swelling. Hence, the longitudinal swelling is not only influenced by setting strain or the setting time, but the number of bonds initially accessible.

More recently, the absorption of water by different keratins has been explained by Lynch and his co-workers (19). They explained that the two hydrophilic groups, amino ($N--H_3^+$) and carboxyl ($-COO^-$) ions, account for the greater part of absorption at low humidity. Above 5% ~~R.H.~~ v.h., water is probably associated with the peptide groups of the main chains, thereby facilitating structural rearrangement which occurs with increasing ease as the water content increases. Beyond 80% R.H. the content of absorption is dependent on constraints to swelling of the fibre structure. They further observed, that the keratin which has peptide hydrolysis or cystine reduction absorbs more water at high humidity, while the introduction of bulky molecules to the keratin decreases the absorption (1, 2, 5) of the water.

Table. 4.2

4.3.3 INSIDE FORMIC ACID (CONCENTRATION = 95%

VOLUME SWELLING (%)

Time in minute	Merino	Cross	Yankasa
1	152.8	159.21	143.36
2	144.9	153.45	156.0
5	140.3	149.64	162.44
30	137.2	151.22	169.44
60	135.6	143.36	180.56
120	131.0	143.36	185.27
180	131.0	143.05	188.15

4.3 Formic Acid (concentration = 50%)

2	80.40	84.98	56.25
5	79.06	81.71	58.76
30	80.90	81.98	57.50
60	80.90	81.71	57.50

SWELLING IN FORMIC ACID

The swelling of different wools inside aqueous formic acid is given in the table (4.2). Acetic acid and HCl also behave in the same way but the maximum swelling of the wool in formic acid is achieved in one minute. It appears, with regard to swelling, that formic acid is unique only in the rapidity with which it penetrates the wool fibre.

Feughelman (23), Sæpåkman (24) and Szucht (23) had thoroughly studied the effect of formic acid upon the swelling of wool. According the finding by Bendit (26), there is still a significant fraction of the helical form present even in 100% formic acid, at least half or more of them. Feughelman (23) had observed that there was contraction in length when wool fibre is immersed in formic acid; and the contraction was maximum when concentration of the formic acid was 70%. To explain the behaviour of wool in side the formic acid solution, two explanations were given by Feughelman (23). He proposed that the microfibrils were distorted from a linear arrangement as the matrix swells around them, causing a decrease in the microfibril length. Another possibility was that the formic acid might be responsible to the super-contraction of the - helices which can then exert an appreciable internal tension on the fibre until concentrations of acid were reached inside the fibre which were high enough

to allow the swelling forces overcome the super contraction phenomena.

There seems to exist good relationship between the sulphur content of wool and the maximum radial or volume swelling of the fibre (26) in 95% formic acid.

Table. 4.4

Wool	Concentration of ½ cystine/1000g.	% Radial Swelling in 95% formic acid
Merino	111	52
Cross	102	56
Yankasa	89	69

The above table shows that, in general, swelling of the wool fibre decreases with the increase of cystine content. Probably, the wool containing more sulphur introduces additional disulphide cross-links into the matrix, which limits its ability to swell in the formic acid. The consideration importance of disulphide bonds in limiting the swelling in formic acid has been shown in recent studies with partially reduced wool fibres in which it was found that a strict inverse relationship exists between the number of disulphide bonds remaining in the fibre and the extent of swelling (26,27). This relationship holds for the results quoted above.

4.3.4 The maximum swelling of different fibres in different solvents may be summarised as follows:-

Yankasa wool > Merino > Cross in water

Yankasa wool > Cross > Merino in HCl (0.7%), formic acid (95%), Formamide, Phenol (10%), Phenol (90%), formaldehyde (40%)

Cross wool > Yankasa wool > Merino in Formic Acid (50%)

Cross wool > Merino > Yankasa ~~Cross~~ in Dimethyl formamide (5)%).

Urea (50%), Hydrazine (90%).

It has been observed, in general, that anhydrous media are less effective than aqueous ~~aquences~~ media. For example, glacial acetic acid shows no swelling, but the same acid when diluted to 50% gives a marked swelling. Due to the presence of water, the solvent is accommodated at certain preferred sites.

The different rates of swelling by different fibres are due to structural differences, as reported in the next chapter. There is a marked difference in the amino acid composition of different fibres. The Yankasa wool behaves quite abnormally which is not unexpected in view of the difference in amino acid composition and structure. The different rate of diffusion is another possibility, giving rise to different rates of swelling.

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Chapter 5

5.0 PH WORK

5.1.1 Titration Curves of Proteins:

In the titration curve of an amino-acid of structures

$$R - CH(NH_2) - COOH$$

the combination with acid or base increases with decreasing or increasing pH respectively. The position of the curve on the pH axis is defined accurately by the pK values of the carboxyl and amino groups. Thus one equivalent of glycine, in the iso-electric state, will combine with one equivalent of hydrochloric acid, the pH of half combination being 2.34, and with one equivalent of sodium hydroxide, the pH of half combination being 9.60.

The transition from an amino acid to a peptide brings about a considerable change in the ionising properties of the carboxyl and amino groups. In glycylglycine, the pK values are considerably displaced from those of glycine, viz pK_1 of carboxyl is 3.06 and pK_2 of amino is 8.13. The curve has been displaced, therefore, towards neutrality by approximately 0.7 pH units on the acid side and 1.4 units on alkaline side. It is obvious that the curve of glycylglycine could not be theoretically determined from a knowledge of the pK - values of glycine.

In a mixture of amino acids each acid is titrated with acid or base in its pH range and if the pK values of the components are sufficiently far apart their regions of titration are distinct. The presence of phenolic, sulphydryl, imidazole or guanidinium groups considerably complicates the interpretation of a titration curve, as the regions of titration of these groups tend to mask the titration of amino and carboxyl groups and render them indistinct, e.g., histidine contains an imidazole group (pK 6.00) which titrates in the unbuffered region between an amino and a carboxyl group titration, similarly the guanidinium group of arginine (pK 12.48) which titrates in the upper regions of an amino group titration rendering the pH of maximum combination indistinct or invisible.

The different groups titrating in a protein show a similar overlapping due to the closeness of their pK values and a continuous curve is obtained rather than one indicating each titration as discreet step.

5.1.2 Dissociation of Amino Acids:

In explaining the dissociation properties of an amino acid it is obviously necessary to consider two or more different dissociable groups. The dissociation constants of these groups can be measure directly by titration.

Experimetally Measured Logmithmic Dissociation Constants of Some Amino Acids:

Simple Amino Acids

Amino Acids	pK_1 ($-COOH$)	pK_2 ($-NH_3^+$)	Isoionic Point (pI)
Glycine	2.34	9.60	5.97
Alanine	2.34	9.69	6.00
Valine	2.32	9.62	5.96
Leucine	2.36	9.60	5.98
Isoleucine	2.36	9.68	6.02
Serine	2.21	9.15	5.68
Proline	1.99	10.60	6.30
Phenylalanine	1.83	9.13	5.48
Tryptophan	2.38	9.39	5.89
" " Methionine	2.28	9.21	5.74

Amino Acids Containing Also a Phenolic or Sulphydryl Group

	pK_1 ($COOH$)	pK_2	pK_3	pI (Iso-ionic point)
Tyrosine[2]	2.20	9.11(NH_3^+)	10.9(OH)	5.66
Diiodotyrosine	2.12	6.48(OH)	7.82(NH_3^+)	4.29
Cysteine	1.96	8.18[2]	10.28[2]	5.07

Amino Acids Containing Two Carboxyl Groups

	pK_1 (-COOH)	pK_2 (COOH)	pK_3 (NH_3^+)	pI(Iso-ionic point)
Aspartic Acid	1.88	3.65	9.60	2.77
Glutamic Acid	2.19	4.25	9.67	3.22

Amino Acids Containing Two Basic Groups

	pK_1 (COOH)	pK_2	pK_3	pI(Iso-ionic point)
Histidine	1.82	6.00 (M^+)	9.17(NH_3^+)	7.59
Arginine	2.17	9.04(NH_3^+)	12.48( )	10.76
Lysine	2.18	8.95(α-NH_3^+)	10.33(-NH_3)	9.74

5.1.3 Binding of Ions by Proteins:

The precipitation of proteins from aqueous solution by certain complex acids, such as trichloroacetic acid and phosphotungstic acid, can be regarded as the formation of a salt, the protein acting as the cation and the acid providing the anion according to the reaction $P^{n+} + nA^- \rightarrow PA_n$.

Other examples of anions which form protein precipitates (and in some cases precipitates with certain amino acids) are picric acid, flavianic acid, picrolonic acid. Many proteins also form insoluble precipitates with certain heavy metal cations, such as Ag^+, Zn^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, and Au^{3+}. In such cases the

precipitation may be regarded as the formation of an insoluble unionized salt in which the protein serves as the anion.

$$P^{n-} + n\,M^{+} \rightarrow M_nP$$

The metal ions forming such precipitates are frequently polyvalent and are known to form many insoluble salts.

These examples are obvious cases of ion binding by proteins. More subtle cases have come into prominence more recently. In 1941 - 1942, Steinhardt and co-workers published the results of a series of investigations of the behaviour of wool fibres and ovalbumin solutions when titrated with various strong acids. On the basis of the simple theory concerned only with the binding of protons, the titration curves, which are plots of H^+ bound to protein versus pH, should be independent of the acid used. Such was not the case. The curves for different acids had the same general shape, but were shifted along the pH axis. Since the protein groups being titrated in this pH range are essentially the carboxyl groups, the obvious conclusion is that the dissociation constant of the carboxyl groups depends on the nature of the acid added, or on the nature of the other anions in the solution. Steinhardt et. al, presented an explanation of the results on the basis that anions are also bound by the protein so that it is necessary to consider the dissociation constants of new groups, the protein - anion complex groups.

Protein HA $\rightleftharpoons$ Protein A^- + H^+ as well as Protein -H $\rightleftharpoons$ Protein $^-$ + H^+

Assuming the curve with HCl to be the normal one, the affinity of the various anions can be obtained according to the magnitude of the shift in the titration curve. The results show that anionic dyes have strong affinities as is to be expected.

Perhaps a somewhat more rational explanation of the effect of the bound anions on the titration curve can be given in terms of the electrostatic interaction term - 2zw/2.303, in the low pH titration region the protein possesses a net positive charge which is diminished by anion binding. Thus, the greater the degree of binding, the smaller z and the less important the electrostatic term.

The net effect will be to enhance hydrogen ion binding at a given pH, as is observed.

5.1.4 The Isoelectric and Iso-ionic Points of Wool:

The amphoteric nature of wool was proposed by Speakman and Hirst (1), Elod (2), and in particular was demonstrated by the complete acid-base titration curve obtained by Speakman and Stott(10). To study the mechanism of acid-base titration they tried to obtain the isoelectric point. The isoionic point of a protein is that pH at which it carries no net covalently bound positive or negative charge. The isoelectric point is that pH at which the protein does not migrate toward either the anode or the cathode in an electric field. So far as the total net charge on a molecule is expressed by the binding of protons, the term isoelectric is applicable to the term in which the net binding of protons is zero.

Earlier attempts made by different workers are given in the table below. There are variations in the results because the pH at which the net charge, including bound ions, is zero depends on the nature and concentration of ion in solution.

The isoelectric point of Wool determined by various methods

Methods	Isoelectric Point and References
Ferricyanide absorption	4.9 Speakman (3)
Swelling minimum	4.9 Elod and Silva (4)
Swelling minimum	4.0 Meunier and Ray (4)
Acid absorption	3.4 Manston (6)
Microelectrophoresis	3.4 Marris (7)
Titration curve	5.0 Speakman and Hirst (1)
Electrophoresis	4.9 Dumanskii and Dumanskii (9)

In later work on the combination of acids and bases, Speakman (11), suggested the existence of an isoelectric region rather than a point. He observed this region within the range of pH - 4.0 - 8.0, which was also supported by the results of measurements of the swelling and elastic-properties of wool in different aqueous enviroments. In this case, the pH at which there is no net charge, with respect to the binding of protons alone, may not necessarily be the same as the pH at which there is no migration in an electric field. Sorenson first used the term ISOIONIC to refer to the pH at which there is no net charge provided no ions are bound other than protons.

The isoionic point of an insoluble protein has been considered to be the pH value which is approached by prolonged dialysis against water, and also the pH of the equilibrium, which is not altered by the addition of small amounts of neutral salt. On the basis of this definition, Lemin and Vickerstaff (13) determined the isoionic point of wool by measurement of the pH at which addition of salt does not affect the pH. They obtained a value of 6.2 which is approximately the mid point of the isoelectric region. The value obtained by Lemin and Vickerstaff will be approximately correct if the affinities of both cation and anion for wool are very low or nearly equal. The term iso-ionic point is more appropriate than the term isoelectric point in a discussion of the simple proton-binding of amino acids. Actually, the difference in the binding of other ions in case of amino acids is so slight that it is a matter of little importance whether or not one distinguishes between isoelectric and iso-ionic point.

5.1.5. Comparision of the Titration curves of Soluble and Insoluble proteins:

It has been pointed earlier that the mechanism of titration processes in wool and soluble proteins is quite different. The extensive isoelectric region and different effect of salts make these process entirely different. Although the shape of the titration curve for a soluble protein is similar to that of the individual amino acid, and no isoelectric region is evident, the

titration curve is spread over a wider pH range. This may be taken to show that the acid or base tends to increase in strength as the number of combined protons or hydroxyl ions is increased.

When the titration curve of wool obtained by Speakman and Hirst (1) is compared, on a common axis, with that of egg albumin by Kekwick and Cannan (14) major differences are immediately noticed.

As far the composition in respect of those groups which effect the shape and position of their titration curves is concerned, it is very similar in egg albumin and wool, the differences in the titration curves can only be accounted for in terms of differences in solubility.

The most important factors to be considered are:

(1) In the case of wool, the region from pH 6-10 is excluded where acid or base combining capacity is very small.

(2) The amounts of acid of base bound by the insoluble protein increase sharply towards the extremes of pH, although the maximum combining capacity is reached at approximately the same pH value as in the case of the soluble protein. Hence, the titration curves are steeper than those of soluble proteins.

(3) The pH of half maximum combination of acid or base is a direct measurement of the dissociation constant of the groups present in simple substance. Soluble proteins

are found to have a pH of half maximum combination with acid of at pH 4, whereas wool has been shown to be half combined with acid at pH 2.3 (1,10,15).

Cannan (16) tried to explain the titration curve of egg albumin by the application of the law of mass action to the absorption of acid. He used a single dissociation constant to describe all the reactant groups. The same expression can not be applied to the combination of wool with acid, without certain modifications (17).

The difference between the titration curve of soluble and insoluble proteins also lies in the difference of their effective molecular size. Only a limited number of free hydrogen ions can combine with an insoluble protein as the potential thus acquired excludes the further penetration of protons. As the radius of the fibre decreases, the potential produced by a given charge also decreases but the number of groups capable of accepting a charge increases with the cube of the radius. Hence, the potential is proportional to the square of the radius for a given amount of protons combined per unit volume of the wool. Moreover, there is a possibility of entry of anions into the wool, during the titration, which is one cause of the difference between the behaviour of wool and of the soluble protein.

5.1.6 Maximum Capacity of Wool for Acids and Alkalies:

Wool contains carboxyl groups ionised at the isoionic point, their charges being neutralised by positively charged basic groups, mainly amino and guanidinium groups. The carboxyl groups are converted to the undissociated form ($COO^- + H^+ \rightarrow COOH$), by acid. The number of equivalent acid groups necessary to back-titrate wool from the isoionic point to this limiting value is known as the maximum acid combining capacity of wool. This quantity gives not only the number of carboxyl groups in the wool which were charged at the isoionic point, but also the number of positively charged basic groups, since these are equivalent.

Similarly when wool is immersed in alkaline solution, the ionisable groups of wool are brought to the basic form. However, it is observed that to reach a stage where all the groups are in basic form is impossible because the pk-value of the guanidinium group is very high. There is always the possibility of irreversible modification of peptide links and disulphide bonds at high pH values, and ionisation of phenolic residues.

The maximum capacity of wool for acids is remarkably constant. The capacity of wool for inorganic acids is usually considered to lie in the range 0.81 and 0.87 m.eq per gram of wool (1,17,21).

The amount of alkali bound by wool is less definite (17,22, 23,24). This is because (a) the high pH required for complete titration of the arginine residues causes extensive hydrolysis of

amide and peptide groups, (b) the disulphide groups undergo hydrolytic and other reactions in alkaline solution.

For determining, directly, the alkali-binding capacity of wool McPhee (25) has devised a method based on his observation that high salt concentrations protect wool from alkali degradation without preventing reaction with ionizing side-chain groups. He obtained a value 1.2m-eq per gram for the alkali capacity.

Another explanation put forward by Vickerstaff and Speakman(18) was that the shift in the acid branch of the titration curve of insoluble proteins relative to the soluble or model protein is due to the positive charge on the molecules and not to any real change in the pk values of the carboxyl groups. Similarly the shifting of the alkaline side of the curve must be attributed to the effect of negative charge on the molecules created by the removal of proteins by hydroxyl ion.

The sharp discontinuity of potential at the fibre surface is due to the electrical double layer which surrounds all colloid systems in solution. The double layer surrounding the wool fibre will have a considerable effect on the titration curve, particularly when small amounts of hydrogen ion are combined. The simple double layer treatment which satisfactorily explains the titration of soluble proteins, has been combined with the general theory of dual entry of ions into an insoluble protein by Alexander and Kitchener (20). When the potential-determining charges on a protein

are separated by a greater distance than of thickness of the double layer, the titration of the fibre becomes similar to that of soluble protein, as the arbitrary distinction between outside and inside has disappeared.

Other theories to explain the difference btween the titration curves of soluble and insoluble proteins have been advanced. The presence of a separate solid phase, a fibre phase, in the titration of the insoluble proteins, could be responsible for some of these differences. This gives rise to the discontinuities which occur at irregular intervals during the titration of sparingly soluble proteins. Earlier workers have postulated the presence of a two phase system but a comprehensive attempt has been made by Peters and Speakman (19) to explain the titration curves of wool keratin in this way.

Speakman (1,10,15) attributed the difference in the titration of soluble and insoluble proteins to the effect of "salt binding" between the molecules of fibrous protein preventing the functioning of their constitutional group unless a very concentrated solution of electrolyte was present to break that binding.

5.1.7 Titration of Wool:

The ionisation of any acid HA can be expressed by the equation (1) in accordance with Brönsted's convention

$$HA \rightleftharpoons H^+ + A^- \qquad \ldots\ldots\ldots(1)$$

the ionisation constant is given by equation (2),

$$K_i = \frac{a_{H^+} \times a_{A^-}}{a_{HA}} = \frac{(H^+) \times (A^-)}{(HA)} \times \frac{f_\pm}{f_u} \qquad \ldots\ldots(2)$$

where a_{H^+}, a_{A^-}, a_{HA} represent activities, ( ) represent molar concentration, $f_\pm$ is the mean ion activity coefficient, and fu is the activity coefficient of the undissociated acid.

Equation (2) may be written by

$$pH = pK' + \log (A^-)/(HA) \qquad \ldots\ldots\ldots(3)$$

where $pH = -\log(H^+) f_\pm$ and $pK' = -\log K_1 \frac{fu}{f_\pm}$

Since $pH = pK'$ when $(A^-) = (HA)$, pK' is the pH value at which the acid is half ionised, i.e. the pH corresponding to the mid point of the curve. It is important to note that pK' changes with temperature (through K_i) and with ionic strength of the medium (through $fu/f_\pm$). At zero ionic strength pK' is denoted as pk_o.

Values of pK' and pK_o for various ionisable groups, as found in the amino acids or in simple peptides are given below, derived from data given by Cohn and Edsall (26,27).

Values of pK'and pK'_o and Heats of Ionisation (ΔH^o) of Ionisable Groups of Wool:

Group	Amino Acid	pK'	pK'_o	ΔH^o (Kcal/mole)
α-carboxyl	end group	3.0-3.2	3.2	1.5
β-carboxyl	Aspartic acid	3.0-4.7	4.0	1.5
γ-carboxyl	Glutamic acid	Ca 4.4	4.0	1.5
Phenolic hydroxyl	Tyrosine	9.8-10.4	10.0	6.0
Sulphydryl	Cysteine	9.1-10.8	10.0	-
Imidazole	Histidine	5.6-7.0	7.0	6.9-7.5
α-Amino	end group	7.6-8.4	8.0	10 - 13
ε-Amino	Lysine	9.4-10.6	10.0	10 - 12
Guanidinium	Arginine	11.6-12.6	12.5	12 - 13

The sulphydryl or thiol group does not occur in significant amounts in perfect wool but its pK' is included, since it has a bearing on the discussion of the results.

According to Vant Hoff's equation ..... (4)

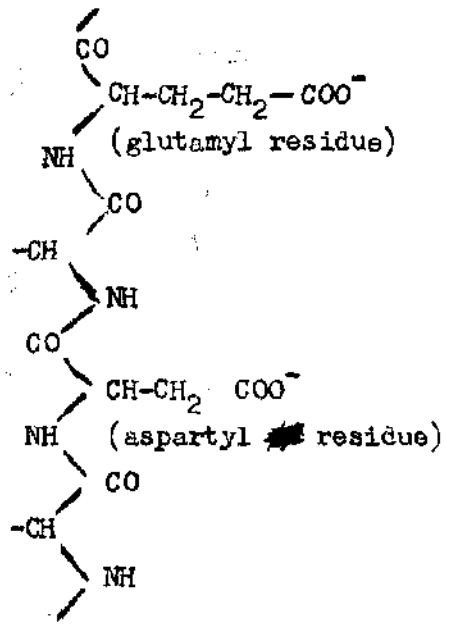
$$\Delta H^o = RT^2 \frac{\ln K}{T} = -2.303\, RT^2 \times \frac{pK}{T}$$ where ΔH^o is the heat of ionisation referred to a certain standard state, R the gas constant, T the absolute temperature, and K the thermodynamic dissociation constant.

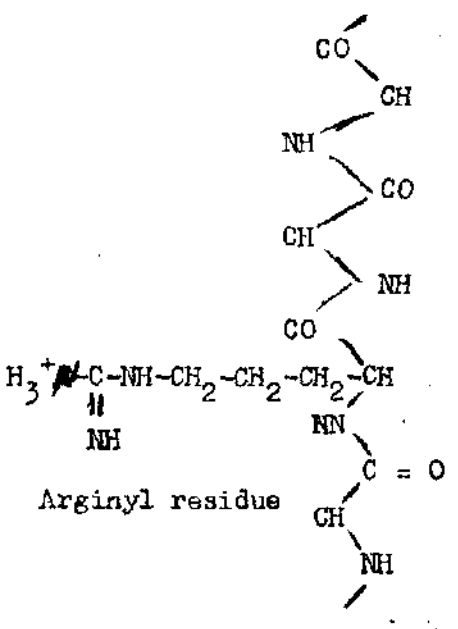
5.1.8 Ionisable Groups of Wool:

The ionisable groups of wool are the acid and basic groups in the side chains derived from various residues, viz., the β- and α-carboxyl groups respectively of aspartic and glutamic acid, not bound as amides, the ε-amino groups of lysine, the guanidinium group of arginine, the imidazole group of histidine and the phenolic group of tyrosine.

According to Speakman (1,2,8,9,10,11) these groups are ionised in virgin wool, as shown below, the attraction between the positively and negatively charged groups constituting what is known as the "SALT-LINK".

In addition, α-carboxyl and α-amino groups at the ends of each polypeptide chain also participate in protons transference:





The amide groups, owing to the extremely low value of their basic constant ($\sim 10^{-20}$), do not accept protons even at low pH value. At pH values below 2, however, some hydrolysis of this group may occur, with liberation of carboxyl groups and ammonium ions.

When wool is immersed in a dilute solution of HCl, the ionisation of the weakily acidic carboxyl groups is depressed, as follows: $RCOO^-.H_3NR + H^+ + Cl^- \rightleftharpoons RCOOH + H_3^+N.R$ .....(5) where R is the bulk of the wool molecule.

This back titration of carboxyl groups must be accompanied by the absorption of an equivalent number of chloride ions in order to avoid building up a large electrostatic potential on the fibre.

Similarly, in alkaline solutions, effects such as the irreversible modification of disulphide bonds being for the moment ignored, the hydroxyl ions capture protons from the charged amino, imidazole and guanidinium groups, and from the phenolic hydroxyl group, the electrostatic potential created by the carboxyl groups and the phenolate ion being neutralised by absorption of cations in accordance with the following scheme:

$RCOO^- + H_3N^+.R + Na^+ + OH^- \rightleftharpoons RCOO^-Na^+ + H_2NR + H_2O$ .....(6)



From the definition of pK and pH it is obvious that the pK value of an ionising substance is a pH at which half the available groups are ionised, e.g., in the titration of a soluble amino acid with HCl the pH of the solution in which the carboxyl group is 50% dissociated in the pK of the amino acid. This simple relationship exists because of the back significant association between chloride ions and charged amino groups. When an insoluble protein is titrated, however, the combination of protons must be accompanied by the adsorption of anions and the pK of the reacting group will be significantly affected. For example, in case of HCl combining with wool it has been assumed (31,32) that an equal number of anions and protons are combined and, therefore, the pK of the reacting group is twice the pH of half combination.

pK also varies with the temperature and ionic strength of the medium, pK_0 being the value of pK at zero ionic strength. The different values of pK of various groups found in wool protein are given on page 108 These values have been determined from the measurements in simple peptides and are necessarily only incorporation of amino acid into the complex structure of a polypeptide may significantly alter the pK values of the ionising group due to interaction with the adjacent polar group (33).

From the titration data the relationship between the number of protons bound to the wool and the pH of solution is obtained. The pH is measured directly but the number of protons are obtained

by calculation. It is convenient to select a starting point for titration near the neutrality (at iso-ionic point of the wool), and to consider the acid side in terms of hydrogen ions and to the alkaline side in terms of hydroxyl ions. Actually the combination of hydroxyl ions is not with the proteins but with protons removed from it. The bound ions are calculated by the difference between the total quantity of the ion added, less the amount remains free in the solution.

5.1.9 Theoretical Approach to Acid Base Titration

5.1.9.1 (a) The Steinhardt - Harris Theory:

The titration curves of wool with a variety of strong acids, including sulphonic, carboxylic and phenolic aromatic acids have been studied by Steinhardt, Fugitt and Harris (34 - 39). Their results indicate that as the molecular weight of the acid increases, the titration curve is displaced to higher pH value. The same effect is observed when neutral salt was added. Steinhardt and Harris, who evolved the first detailed theory, postulated that the combination of acids with wool can be resolved into two partial reactions; one with hydrogen ion and the other with the acid anion, each reaction being governed by its own equilibrium constant.

They made three main assumptions in obtaining a theoretical relationship between pH and acid absorption:

(1) both hydrogen ion and anion combine with the wool proteins according to the law of mass action or the Langmuir adsorption law.

(2) no recognition need be taken of differences in hydrogen ion concentration inside and outside the fibre.

(3) variation in activity coefficients in the fibre phase may be disregarded.

They consider the equilibria and mass action equations

$$W^{\pm} + H^{+} \rightleftharpoons WH^{+},\ K_H = \frac{\left[W^{\pm}\right]\left[H^{+}\right]}{\left[WH^{+}\right]} \qquad \ldots\ldots\ldots(7)$$

$$W^{\pm} + A^{-} \rightleftharpoons WA^{-},\ K'_A = \frac{\left[W^{\pm}\right]\left[A^{-}\right]}{\left[WA^{-}\right]} \qquad \ldots\ldots\ldots(8)$$

$$WH^{+} + A^{-} \rightleftharpoons WAH,\ K_A = \frac{\left[WH^{+}\right]\left[A^{-}\right]}{\left[WHA\right]} \qquad \ldots\ldots\ldots(9)$$

$$WA^{-} + H^{+} \rightleftharpoons WHA,\ K'_H = \frac{\left[WA^{-}\right]\left[H^{+}\right]}{\left[WHA\right]} \qquad \ldots\ldots\ldots(10)$$

where $K_H \cdot K_A = K'_H \cdot K'_A$ and where $W^{\pm}$ etc., represented various states of wool molecule, $W^{\pm}$ being analogous to $H_3^{+}NRCOO^{-}$, WH to $H_3^{+}N.RCOOH$, and WHA to $AH_3.N.RCOOH$. In order to account for the

near equivalence of anion and cation uptake it was assumed that

$K'_A \gg K_A$ and $K_H \gg K'_H$

If A is the amount of acid bound by the wool and A_m is the amount bound when the wool is saturated with acid.

$$\frac{A}{A_m} = \frac{[WHA] + [WH^+]}{[WHA] + [WH^+] + [WA^-] + [W^+]} \quad \ldots\ldots\ldots(12)$$

Substituting from the equation (9) to (11)

$$\frac{A}{A_m} = \frac{1}{1 - \frac{1}{a_H}\left(\frac{a_A + K'_A}{a_A + K_A}\right)} \quad \ldots\ldots(13)$$

where a_H and a_A are the activities of H^+ and the anion A^- in solution. When $A''A_m = \frac{1}{2}$, that is, at $pH\frac{1}{2}$, and when $K'_A \gg a_A \gg K_A$, equation (13) reduces to $pH\frac{1}{2} = pK'_H + \log a_H - \log K'_A$ .....(14)

Equation (14) provides a satisfactory explanation for the experimentally determined relationship between $pH\frac{1}{2}$ and anion concentration for solutions of low ionic strength.

Further, from equation (13), when $K'_A \gg a_A \gg K_A$

$$\frac{A}{A_m - A} = \frac{1}{\frac{K'_H}{a_H}\left(\frac{a_A + K'_A}{a_A + K_A}\right)} \simeq \frac{a_H \cdot a_A}{K'_H \cdot K'_A}$$

and $$\log \frac{A}{A_M - A} \simeq -pH - \log K'_H . K'_A + \log a_A \quad \ldots\ldots\ldots(15)$$

With no added salt $a_H = a_A$, hence $\log \frac{A}{A_m - A} \simeq 2\ pH - \log K'_H \cdot K'_A$ ..(46)
On plotting $\log (A/A_m - A)$ against pH, these equations give slopes of -1.0 and -2.0, whereas measured values are -0.5 and -1.0 respectively.

To overcome this considerable and uniform difference, and to fit experimental data Steinhardt (38) introduce the square roots of activities and dissociation constants as parameters in his equations, but this has no theoretical basis.

5.1.9.2 Criticisms of the Steinhardt - Harris Theory:

Peter and Speakman (40) criticized the theory for its application of the mass action law to the formation of ionic complexes which they consider are not real. The fault in the Steinhardt - Harris theory lies in the assumption that both anions and cations react at a single site. Regarding Peter's and Speakman's second criticism for its neglect of differences in ion concentration inside and outside the fibre, it follows that the binding of ions in a solid phase in equilibrium with a liquid phase will be unaltered by the presence of a second liquid phase with which both are in equilibrium. Contrary to this explanation, in the hydrolytic and other catalytic effects of H^+, OH^- or other ions; the internal solutions cannot be ignored.

5.1.9.3 The Gilbert - Rideal Theory (41)

In 1944, Gilbert and Rideal (41) attempted to explain the interaction of acids and absorption of acids by wool. In that theory it is assumed that there are equal numbers of positive and negative sites on the wool fibre in accordance with the salt-link theory and an anion is free to occupy any positive site that is not occupied already by an anion and that this freedom is not affected by its position relative to charged or uncharged carboxyl groups.

The theoretical development of Gilbert and Rideal is based on the expression derived by Fowler and Guggenheim (42). They have shown that the chemical potential or partial free energy μ of an uncharged substance distributed at random among a limited number of similar sites is given by:

$$\mu = \mu^{o}\ (T,P)\ \text{fibre} + RT \ln \frac{\theta}{1-\theta} \quad \ldots\ldots\ldots (17)$$

where θ is the fraction of sites occupied and μ^{o} is the value of μ when half of the sites are occupied. If μ_H is the chemical potential of the hydrogen ions in solution, μ^{o}_{H} the partial molar free energy of the hydrogen ions at unit activity and a_H, the activity at some other concentration, then

$$\mu_H = \mu^{o}_{H}\ (T,P)\ \text{fibre} + RT \ln \frac{b}{1-\theta} + \psi F \quad \ldots\ldots\ldots (18)$$

and for the solution

$$\mu_H = \mu^\circ_H\ (T,P)\ \text{sol.} + RT.\ln f_H.\left[H^+\right] \quad \ldots\ldots\ldots(19)$$

Where $\mu^\circ_H(T,P)$sol. is the chemical potential of H^+ when the activity at temp T and pressure P is unity and f_H is the activity coefficient. If $\Delta\mu_i = \mu_i^\circ(T,P)$ fibre $- \mu_i^\circ(T,P)$ solution, on equating the chemical potentials at equilibrium inside and outside the fibre, Combining (18) and (19), and writing $\Delta\mu_H$ for $\mu^\circ_H(T.P)$ fibre $- \mu^\circ_H(T.P)$sol.

$$RT \ln \frac{\theta_\mu}{1-\theta_H} = -\Delta\mu_H + RT \ln f_\mu.\left[H^+\right] - \psi F \quad \ldots\ldots\ldots(20)$$

Similarly for monovalent anion

$$RT.\ln \frac{\theta_A}{1-\theta_A} = \Delta\mu_A + RT\ \ln f_A.\left[A^-\right] + \psi F \quad \ldots\ldots\ldots(21)$$

Adding Equations (20 and (21)

$$RT \ln \frac{\theta_H \cdot \theta_A}{(1-\theta_H)(1-\theta_A)} = -(\Delta\mu_H + \Delta\mu_A) + RT \ln f_H \cdot \left[H^+\right].f_A.\left[A^-\right] \quad \ldots(22)$$

Assuming that the total number of basic and acidic sites in wool are equal and that equivalent amounts of anion and cation are absorbed at any one time $\theta_H = \theta_A$

Hence, for a pure acid

$$\log \frac{\theta_H}{1-\theta_H} \simeq pH - \frac{1}{4.6RT}\ (\Delta\mu_H + \Delta\mu_A) \quad \ldots\ldots(23)$$

or at constant anion concentration

$$\log \frac{\theta_H}{1-\theta_H} \simeq -\tfrac{1}{2}pH - \frac{1}{4.6RT}(\Delta\mu_H + \Delta\mu_A + \tfrac{1}{2}\log\left[A^-\right] \quad \ldots\ldots(24)$$

and for low ionic strength: $pH_{\frac{1}{2}} \quad \log\left[A^-\right] - \frac{1}{4.6RT}(\Delta\mu_A + \Delta\mu_A) \ldots(25)$

The following linear relationships are predicted,

(1) In presence of salt, when $\mu_H = \mu_A$, and assuming unit activity coefficient

$\log \theta_H/(1-\theta_H) = pH - \log K$, i.e., a straight line of slope = -1.

(2) In presence of salt, when $\mu_H \neq \mu_A$ but μ a is constant

$\log \frac{\theta_H}{1-\theta_H} = -\log K - \frac{1}{2}\log\left[A^-\right] - \frac{1}{2}pH$ i.e, a straight line of slope = -0.5.

(3) At half saturation, when $\frac{\theta}{1-\theta} = 1$

$pH = \log\left[A^-\right] - 2\log K.$

These predictions are well fitted when applied to Steinhardt and Harris's (35) results for HCl absorbtion alone and in presence of varying amounts of salt.

The main draw backs of Gilbert and Rideal theory are however:

(a) again the graph predicted by equation 18,19, is not exactly linear but sigmoidal, though its slope is very near to the predicted value -1

(b) the linear relationship predicted by equation (~~12~~ 20), the ~~relationship~~ between log $\theta/(1 - \theta_{H})$ and $[H^+]$ is more or less linear on the assumption of constant ionic stength and activity coefficient as unity. Though it is found to hold for low salt concentration, is not fitted for high concentration.

5.1.9.4 Criticisms of the Gilbert-Rideal Theory:

Peters and Speakman (40) have criticized the Gilbert-Rideal theory because equation ~~17~~ 25 suggests that there is no limit to displacement of $pH_{\frac{1}{2}}$ with increasing salt concentration.

Peters (43) has further criticized Gilbert Rideal theory because the experimental value for $\frac{\Delta\mu_H + \Delta\mu_{Cl}}{2.3RT}$ is quite different from the calculated values obtained from the data of Olofsson (44) and Steinhardt and Harris (34, 35).

5.1.9.5 Application of Donnan Membrane Theory: To Peters and Speakman Theory:

Peters and Speakman (40) assuming that the external solution and that as a result of preferential adsorption of H^+ at low acid concentration, the fibre is at a potential ϕ, assumed to be constant over the whole internal volume v. It was also assumed that the anions and cations entering the fibre are equivalent to maintain

potential ψ constant.

Applying the law of mass action:

$$K_H\ (\psi_{W.COOH}) = (\psi_{W.COO^-})\ (H^+)$$

$$(\psi_{H^+}) = (H^+)/\lambda$$

$$(\psi\ A^-) = \lambda\ (A^-)$$

where K_H is the dissociation constant of the carboxyl groups, and

λ is constant $= \left[\ldots \exp.(\psi F/RT)\right]$, and superscript ψ indicates the potential of the solution or solid phase relative to the external solution. ψ indicates the potential of the solution or solid phase relative to the external solution

Applying the Donnan-Guggenheim expression (45) for the electrochemical potential of hydrogen ions in the external solution

$$\mu_H = \mu_H^{o}\ (T) + RT \ln r_H + P\bar{V}_H + RT \ln H \ldots\ldots\ldots (1)$$

where r_H is the activity coefficient and V_H is the partial molar volume of the hydrogen ion at a pressure equal to the mean pressure of the two phases.

In the internal solution

$$\mu_h = \mu_h^{o}\ (T) + RT \ln h - RT \ln r_h + p\bar{V}_h + P\bar{V} \quad \ldots\ldots (2)$$

At equilibrium these are equal, and assuming that $\mu_h^{o}(T) = \mu_H^{o}(T)$ and $\bar{V}_H = \bar{V}_h$ and $P-p = (RT/\bar{V}_w)\ln(w/W)$ where W and w are the activities of water in the external and internal phases and V_w is its partial volume at a pressure equal to the mean of P and p.

$$RT \ln \frac{r_H . H}{r_h . h} + RT . \frac{V_H}{V_w} \cdot \ln \frac{w}{W} = F\psi$$

$$\text{or } \frac{r_H}{r_h} \left(\frac{w}{W}\right)^{r_H} . \frac{H}{h} = \lambda = e^{(\psi F/RT)} \quad \ldots\ldots\ldots(3)$$

where r_H is the ratio of the partial molar volumes of the hydrogen ion and water. The amount of acid combined with the fibre, a', as determined by the difference in the amount originally present and that remaining in the external solution, is given by:

$$a' = v(A^b + h + \Sigma nu) + V(H + \Sigma nU) - (V + v)(H + \Sigma nU)$$

On the assumption that acid is sufficiently strong to give insignificant values of u and v, the expression

$$pH \simeq \frac{z-1}{z} pH_{ext} + \frac{1}{z} \log \left(\frac{a}{v} - H\right)\gamma_{\pm} \quad \ldots\ldots\ldots(4)$$

is obtained where $\gamma_{\pm} = \frac{\gamma_x}{\gamma X} \left(\frac{W}{w}\right)^{r_x}$

Peters and Speakman assumed that the activity coefficients of H^+, X^{z-}, and the activity of water are identical inside and outside the fibre.

The expression for a monovalent acid then becomes

$pH_{int} \simeq 2pH_{ext} - \log \frac{a'}{v}$ as H being small compare with $\frac{a'}{v}$

In the presence of added salt, $pH_{ext} \simeq pH_{int} + \log X$

$$-\log \frac{a}{v} \quad \ldots\ldots(5)$$

For low ionic strength $pH_{\frac{1}{2}} = \log X + \text{constant}$.

Peters and Speakman obtained similar titration curves with HCl and HCl-KCl. When H_2SO_4 was used the result were as good as for the HCl and this strengthened the support for the theory.

Criticisms of Peters and Speakman Theory

Olofsson (21) criticized the theory for its inability to explain the different affinities of various anions for wool. There had been prolonged discussion on this point by Olofsson (21,46,47) and Peters (43,48) despite the fact that Steinhardt et. al. (37) had shown conclusively that different acids, and therefore presumably different anions, have different affinities for the fibre. Peters and Lister (32) and Peters (48) clearly, recognized that anions differ in their affinities for wool, and in the latter paper Peters suggested that his revised model fulfilled both the Gilbert Rideal and Peters-Speakman theories.

5.1.9.6 A Polyelectrolyte Theory of the Combination of Fibres with Acid and Base: (49,50)

The behavior of wool fibre towards acid and base is similar in some ways to that of the soluble and insoluble polyelectrolytes and various theories had been put forward to explain these properties of polyelectrolytes (51,52,53) and the wool fibres (34 - 41). These theories, which are responsible for explaining the electrochemical function of the polyelectrolytes, have been generally based on the use of the electrostatic potential of the polyelectrolytes.

If the simple equation of Henderson-Hasselbalch for a monobasic acid at infinite dilution is considered, then we have: $pH = pK_o - \log (1-\alpha)/\alpha$ where α is the degree of dissociation and pK_o is the dissociation constant of the acid. For the polybasic acid, Bjerrum (54) had introduced the term of free energy (ΔF_v) which is the sum of the energy required to dissociate the proton from the group (ΔF_o) and the energy to remove it (ΔF_i).

Therefore, $\Delta F_v = -RT \ln K = \Delta F_o + \Delta F_i$

if $K = K_o \exp \left[- \Delta F_i/RT \right]$ Then $F_v = -RT \ln K_o + \Delta F_i$ where K_o is the dissociation constant which the dissociating acid group would show, if it was the only ionising group of a molecule corresponding to the basic group of the polymer. Then, the Henderson-Hasselbalch equation becomes for a polybasic acid:

$$pH = pK_o - \log\left[(1-\alpha)/\alpha\right] - (0.4343\Delta F_i/RT) \quad \ldots\ldots\ldots (26)$$

A corresponding equation was put forward by Hartley and Roe (56)

$$pH = pK_o - \log\left[(1-\alpha)/\alpha\right] + (0.4343\chi F/RT) \quad \ldots\ldots\ldots (27)$$

The term χF for electrostatic energy is taken to be ΔF_i, assuming that this was the only significant contribution to ΔF_i. The equations 26 and 27 had been extended by Mathieson and Whewell (44,50) to insoluble wool and nylon fibres. Here, a more detailed account of their theory has been put forward.

Equation 26 for the titration of a polybasic acid can be applied to the titration of a fibre.

positive charges in the fibre due to the fixed charges and C_s is the molar concentration of electrolyte in the external solution, x can be easily calculated.

For titrating by a poly basic acid in the presence of its salt, e.g., sulphuric acid in the presence of sodium sulphate, the corresponding equation will be: $e\Psi/kT = \sinh^{-1} Cf/_2ZC_s$ where Z is the valency of anion, and for an acid in the presence of excess of any poly-valent salt, $e\pi/kT = \sinh^{-1} Cf/2Z_iZ_j$ s where Z_i, Z_j are the valencies of the ions of the salt. For two different acid with anions j and L respectively, $pL_1 \neq pj_1$. Gilbert and Rideal supposed that $pL_1 = pj_1$, presuming the absolute electrical neutrality in the fibre; but equation 28 shows that this is not true for all anions.

When the equation are applied to the acid titration of wool, it is found that pK'_o is independent of salt concentration but varies linearly with degree of dissociation, indicating that two pK's are operating, $pK_q = 3.58$ for paired (salt-linked) groups and $pK_p = 4.855$ for nonpaired groups at 0^oC, present in equal proportions. (Lincoln)

The equation 30 becomes;

$$pH = pK'_q - \log\left[(1-q)/q\right] - (0.4343/RT)(\chi F + \Pi\bar{V}_H + \Delta\mu'^{o}_H) \quad \ldots (35)$$

and $$pH = pK'_p - \log\left[(1-p)/p\right] - (0.4343/RT)(\chi F + \Pi\bar{V}_H + \Delta\mu'^{o}_H) \quad \ldots (36)$$

The equation for the acid titration of a polyampholyte like wool will be:

$$pH = pK'_o - \log\left[(1-\alpha)/\alpha\right] - (0.4343/RT)\ (XF + \Pi \bar{V}_H + \Delta\mu^o_H) \quad \ldots (30)$$

where pK'_o refers to finite concentration.

If pH_1 and pH_2 refer to the fibre phase (internal pH) and to the solution, respectively,

$$pH_2 = pH_1 - (0.4343/RT)\ (XF + \Pi\bar{V}_H + \Delta\mu^o_H) \quad \ldots\ldots\ldots (31)$$

Regarding the titration as taking place only inside the fibre, considered to be uniform, and of constant volume, no electrostatic, osmotic, or 'affinity' work is involved,

$$pH_1 = pK'_o - \log\left[(1-\alpha)/\alpha\right] \quad \ldots\ldots\ldots\ldots (32)$$

Hence, $pH_2 = pK'_o - \log\left[(1-\alpha)/\alpha\right] - (0.4343/RT)(XF+\Pi\bar{V}_H + \Delta\mu^o_H) \ldots (33)$

As explained earlier pK'_o is the intrinsic dissociation constant of the titrating groups in the fibre, whereas the $\Delta\mu^o_H$ is the difference of standard chemical potential in the fibre and the solution. The difference arises only for those acids which have different adsorption in the solution and the fibres or which anions dissociate to different extents in the fibre and in the solution.

To calculate the electrostatic potential for a polyampholyte fibre

$$ex/RT = \sinh^{-1} Cf/_2Cs \quad \ldots\ldots\ldots (34)$$

where x is the electrostatic potential, Cf is concentration of net

Then, K_o represents the dissociation constant of a particular dissociating group of the fibre, and ΔF_i the energy required to transfer a proton from the neighborhood of the dissociating group to the solution surrounding the fibre. According to Mathieson and Whewell, there can be three contributions to ΔF_i, e.i.
(i) an electrostatic contribution χF as a proton adjacent to the dissociating group in the fibre is in a region of potential χ, and is to be transfered to the solution whose net charge is zero; (ii) an osmotic contribution $\Pi\bar{V}_H$ where Π is the osmotic pressure between the fibre and the solution and $\bar{V}_H$ is the partial molar volume of the hydrogen ion and (iii) and"affinity" contribution $\Delta\mu_H^o$, the difference in standard chemical potential of the hydrogen ion in the fibre and in the solution. The complete titration equation for a polyacid fibre is therefore

$$pH = pK'_o - \log\left[(1-\vartheta)/\alpha\right] + (0.4343/RT)(\chi F - \Pi\bar{V}_H - \Delta\mu_H^o) \quad \ldots\ldots(18)$$

where χF is the electrostatic contribution, due to the potential χ and $\Pi\bar{V}_H$ is the osmotic contribution, where Π is the osmotic pressure between the fibre and the solution and $\bar{V}_H$ is the partial molar volume of the hydrogen ion, and $\Delta\mu_H^o$ is the 'affinity' contribution, provided there is any selective adsorption of acid union in the fibre or difference due to the different dissociation in the fibre and the solution.

The value of pK'_o varies within the extreme values of pK'_q and pK'_p, but the same value of pK'_o is obtained for a given value of α for all concentrations of salt. Thus pK'_p and pK'_q could be found, as the extreme values of pK'_o where $\alpha = 0$ and 1.0. If P and q are, respectively, the fractions of the unpaired and paired groups,

$$1-\alpha = P(1-p) - q(1-q)$$

and $pK'_o - \log\left[(1-\alpha)/\alpha\right] = pK'_p - \log\left[(1-p)/p\right] = pK'_q - \log\left[(1-q)/q\right]$

P and q can be obtained as well as pK'_p and pK'_q

5.1.9.8 Comparision to the other Theories:

Gilber and Rideal supposed that all anions in the fibre were specifically adsorbed; whereas Peters and Speakman treated the fibre as possessing a solid phase, analogous to the Donnan membrane, and a liquid phase consisting of the swelling fluid, and calculated an internal pH, which is not measureable, relating to this fluid phase. Mathieson and Whewell's theory takes the fibre as a single phase of known volume and puts more emphasis on the external pH of the solution. The internal pH is used only in the process of the second derivation of the titration equation and refers to the whole fibre.

5.2.1 EXPERIMENTAL

pH Meter

For measurement of pH at constant temperature, a pH meter which can measure with a precision of ± 0.02 pH units is required. A pH meter WG.PYE, model No.290 was used throughout the titration experiments. The pH meter was attached to a glass electrode and a calomel electrode. The usual precautions were adopted to get correct results. All observations for a single curve were at constant temperature, for which a constant bath of 25°C was used throughout this work. The polythene bottles were always kept at that temperature and they were taken out whenever pH was to be determined. The water was wiped off from the side of these bottles before introducing the electrode assembly to measure the pH of the solution.

To standardise the pH meter at the temperature 25°C the standard buffer solutions were used whose pH was being determined at the same temperature. Two types of buffer were used:

(a) 0.05M potassium hydrogen phthalate, (pH=4.0 at 25°C)

(b) a mixture of 0.025M potassium hydrogen phosphate and 0.025M di-sodium hydrogen phosphate (pH = 6.86 at 25°C.

The tests on the electrode assembly using two buffers were always performed before and after each set of observations.

Reagents

For acid titration hydrochloric acid of AR quality and for alkaline titration sodium hydroxide of AR quality were used. The rest of the reagents were also of the same standard.

5.2.2. Purification and Extraction of Wool:

The wools samples were cut off at the ends and roots, followed by successive extraction with ether and alcohol in a soxhlet apparatus, providing 40 syphonings at the soxhlet reservoir in each extraction. The extracted wool was washed in a large quantity of distilled water to remove alcohol and dirt. The wool was further dried with filter paper. It was finally stored in a desiccator containing saturated aqueous ammonium nitrate to give a relative humidity of 65% as near to 25°C as possible.

Prior to the use of the wool it was kept in the desiccator for conditioning at least for a fortnight.

5.2.3 Determination of Iso-Ionic Point:

The iso-ionic points of wools were ascertained by the method used by Lemin and Vickerstaff (13) which is based on the measurement of the pH values of a series of acid and alkaline solutions in equilibrium with wool in the absence of a small amount of a neutral salt. If the equilibrium pH value is in the neutral region, the shift of pH due to the addition of salt varies linearly with

the internal equilibrium pH value. The iso-ionic point is the pH value which corresponds to zero variation in pH, and can be accurately determined by simple extra-polation.

Duplicate samples of conditioned wool (exactly one gram) were placed in 100 cm^3 conical flasks together with 50 cm^3 of hydrochloric acid or sodium hydroxide solution of pH value between 3.0 and 10.0. In each flask, 0.1 g. of sodium chloride was added, then shaken vigorously and maintained for three to four days at 25°C (± 1°C) with containuous shaking. The pH values of the solutions were determined potentiometrically and the changes in the pH calculated. A PYE pH meter model No.290 was used, which was calibrated against Potassium hydrogen phthalate buffer (0.05M at 25°C is 4.01 pH).

The results of a typical experiment are shown in the tables No. 5.1, 5.2, 5.3 for three varieties of wool. When Δ pH was plotted against final pH values in absence of salt a straight line was obtained (Fig. 5.1.1) and this line cuts the pH axis at a value corresponding to a definite pH value. This is defined by Lemin and Vickerstaff as an iso-ionic point (13).

5.2.4 Adjustment of the Initial pH of the Wool at the Iso-ionic Point:

It is necessary to adjust the pH of the wool to its iso-ionic point before the actual determination of the acid and base-combining capacity of the fibres. The pH of the wool was adjusted

by immersing batches of the wool in large volumes of a very dilute solution of hydrochloric acid. After keeping the wool in the acid for 24 hours, it has removed and washed in successive large volumes of distilled water until the recorded pH value is exactly the pH of the iso-ionic point. Finally the wool was then removed, dried by the filter paper and stored at 65% RH, and at 25°C in a desiccator containing saturated aqueous ammonium nitrate.

5.2.5 Determination of the Acid Combining Capacity of Wool:

One gram (± 0.001 g) samples of conditioned wool were taken in 12 different polythene bottles. In each bottle 50 c.c.^{3} of hydrochloric acid of different strengths (pH range 0.1 to 5.0) was added. Before adding the wool, the concentration of the acid was determined by the standard solution of sodium hydroxide using bromo-phenol blue as indicator or by pH measurement, as appropriate, The pH of the acids which were above 2.0 was determined with a pH-meter. Then a one gram sample of wool was added to each bottle. These bottles were vigorously shaken for few minutes, and allowed to stand for 3 - 4 days to reach the pH at the equilibrium state. Seventy-two hours were regarded as sufficient for equilibrium to be reached. The bottles were shaken occasionally to accelerate the absorption. On the fourth day, the pH values of the solution were determined either by titration of an aliquot of the solution or potentiometrically by the pH meter, as before.

5.2.6 Determination of the Alkali-Combining Capacity of Wool:

One gram (±0.001 g) samples of conditoned wool were taken in 12 polythene bottles. In each bottle 50 cm^3 of sodium hydroxide solution (pH range 9.0 to 13) were added. The sodium hydroxide solution was prepared by diluting carbonate free caustic soda solution with CO_2 free distilled water. The pH of these solution was determined using the pH meter up to pH 11.0, but the pH values greater than this could not be obtained this way. Hence, an aliquot of t e solution was titrated with standard hydrochloric acid solution. After adding wool to each bottle, and shaking vigoroustly, they were kept for three days. On the third day the pH value of the solution was determined either by titration of an aliquot of the solution or with the pH meter.

The amount of acid or alkali combined by the wool at the final pH of the solutions was calculated from the values of initial and final pH-values of the solution. The amounts of acid or alkali combined with the wool were expressed in milli-equivalents of acid or alkali per 100g dry wool.

FIG. 24

DETERMINATION OF ISO IONIC POINT
MERINO WOOL

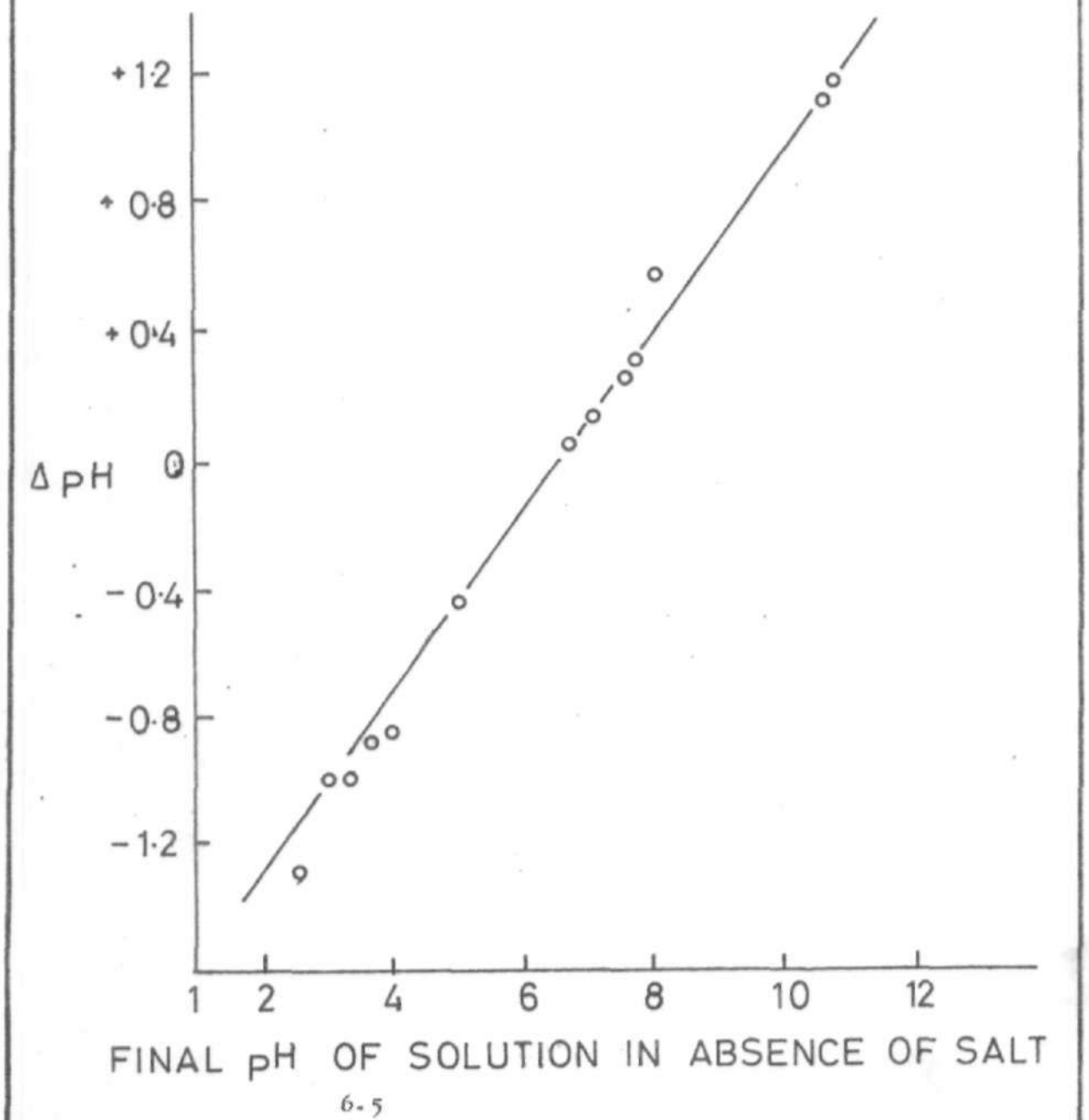


FIG. 25

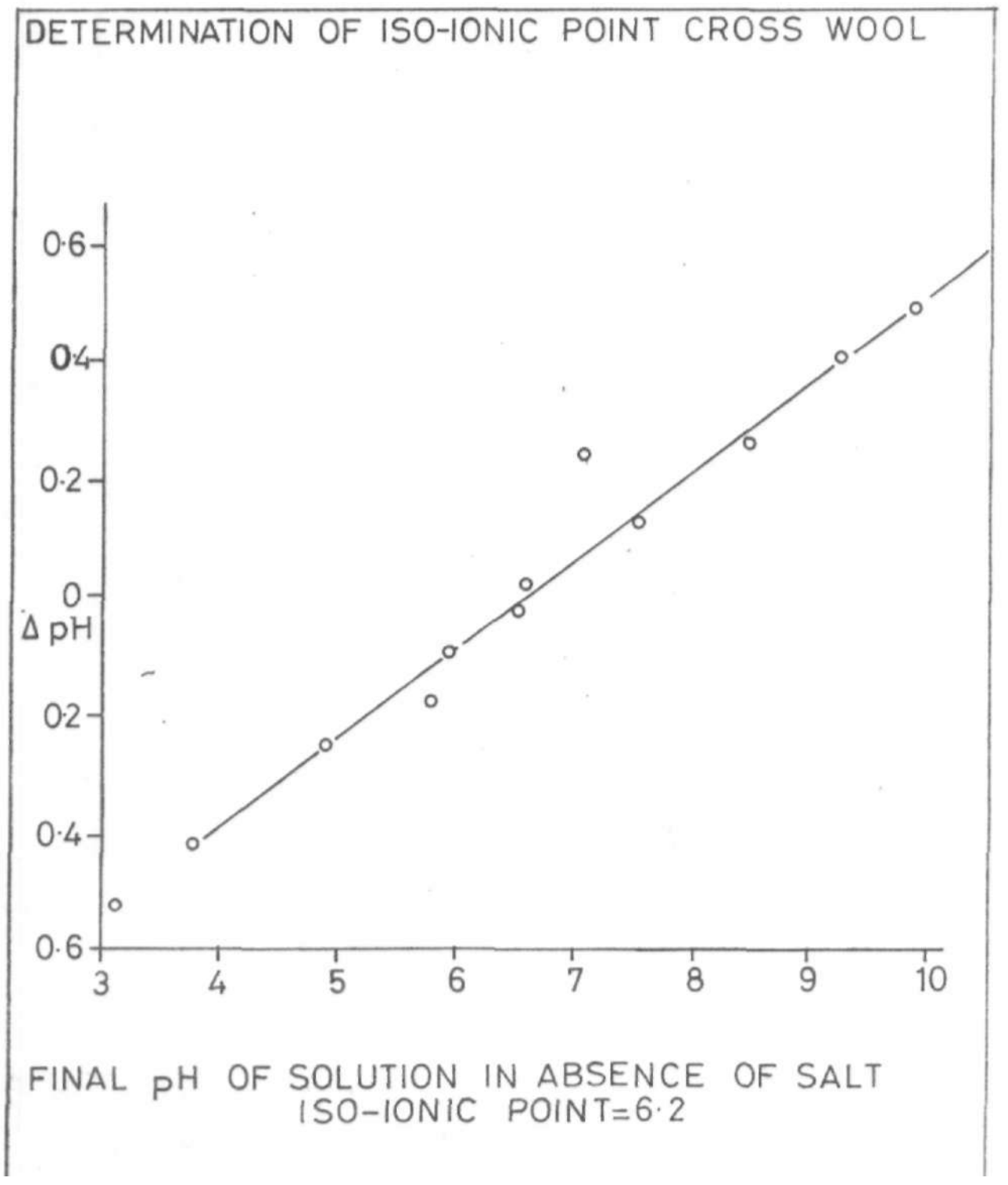

DETERMINATION OF ISO-IONIC POINT CROSS WOOL
0·6
0·4
0·2
0
Δ pH
0·2
0·4
0·6
3
4
5
6
7
8
9
10
FINAL pH OF SOLUTION IN ABSENCE OF SALT
ISO-IONIC POINT=6·2

Table No. 5.1

Determination of Iso-Ionic Point — Nigerian Merino Wool.

Final pH in absence of salt	Final pH in presence of salt	Δ pH
2.60	3.90	-1.3
3.00	4.03	-1.03
3.30	4.30	-1.00
3.70	4.62	-0.92
4.00	4.88	-0.88
5.00	5.45	-0.45
6.75	6.70	+0.05
7.02	6.90	+0.12
7.55	7.29	+0.26
8.00	7.45	+0.55
10.55	9.40	+1.15
10.60	9.42	+1.18

Table No. 5.2

Determination of Iso-Ionic Point — Cross Wool

Final pH in absence of salt	Final pH in presence of salt	Δ pH
3.16	3.67	-0.51
3.78	4.20	-0.42
4.90	5.15	-0.25
5.72	5.90	-0.18
6.58	6.60	-0.02
6.59	6.58	+0.01
7.50	7.37	+0.13
7.04	6.80	+0.24
8.24	7.84	+0.40
9.94	9.44	+0.50

FIG. 26

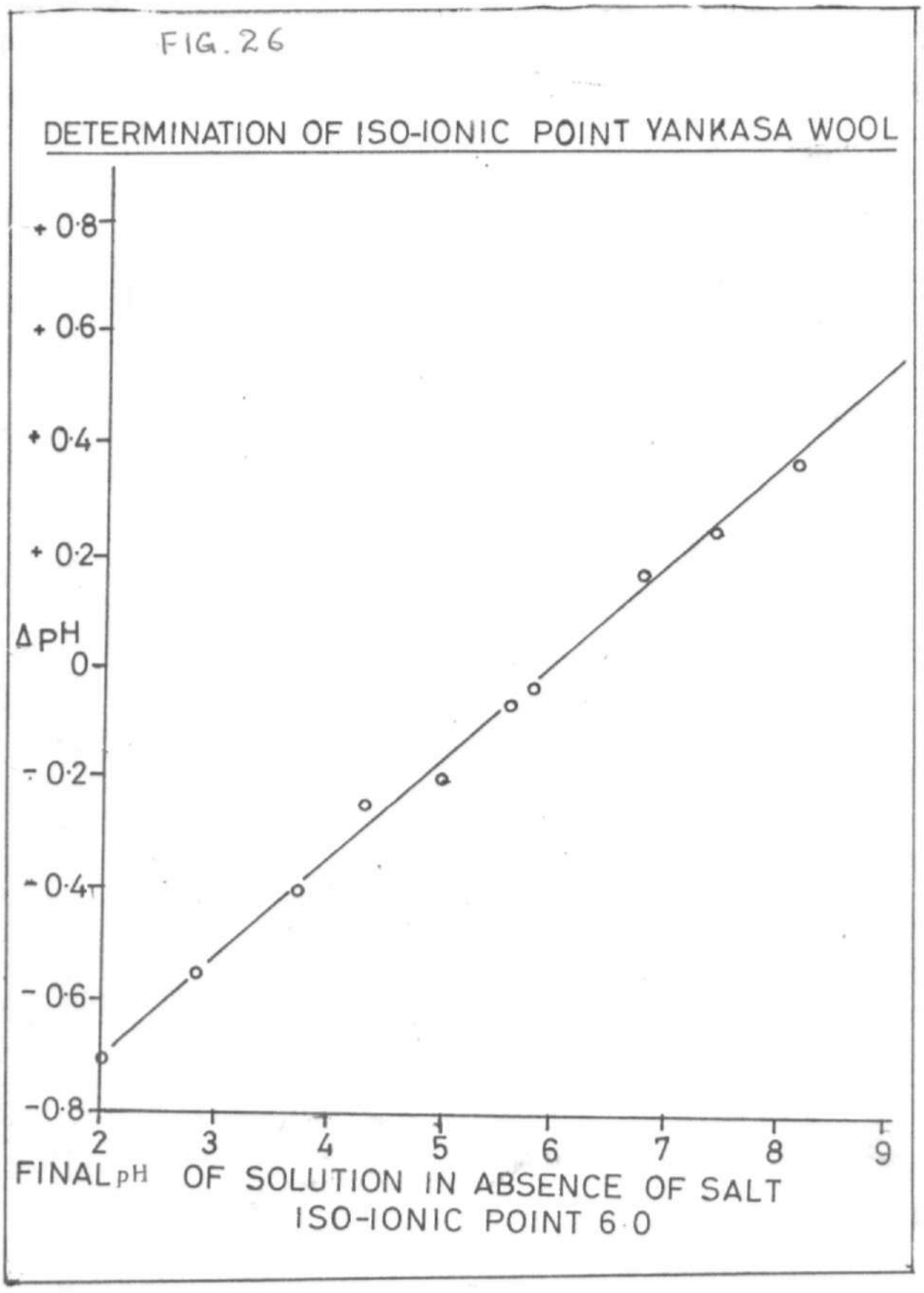

DETERMINATION OF ISO-IONIC POINT YANKASA WOOL
+0·8
+0·6
+0·4
+0·2
ΔpH
0
-0·2
-0·4
-0·6
-0·8
2
3
4
5
6
7
8
9
FINAL pH OF SOLUTION IN ABSENCE OF SALT
ISO-IONIC POINT 6·0

Table No. 5.3

Determination of Iso-Ionic Point Yankasa Wool

Final pH in absence of salt	Final pH in presence of salt	Δ pH
2.00	2.70	-0.70
2.80	3.35	-0.55
3.70	4.10	-0.40
4.30	4.55	-0.25
5.00	5.20	-0.20
5.60	5.66	-0.06
5.80	5.84	-0.04
6.80	6.65	+0.15
7.40	7.15	+0.25
8.10	7.22	+0.38
9.10	8.48	+0.62
9.90	9.18	+0.72

5.2.7 Determination of the Acid and Alkali Combining Capacity in Presence of Sodium Chloride:

In order to study the effect of salt concentration upon the acid and alkali up-take by the wool, another set of experiments was performed. Two different ionic strengths were chosen: 1.0, 0.1. Measurements of the acid and alkali combining capacity were made in the presence of 1.0, 0.1, M sodium chloride. The procedure adopted was similar to that previously described except that the acid and alkali solution in which the wool samples were placed contained 1.0g mol/l, 0.1g mol/l ¹ sodium chloride.

Determination of the Acid and Alkali Combining Capacity in Presence of Divalent Cations Zn(II), Mn(II), Ni(II), Co(II)

Measurements of the acid and alkali combining power were also made in presence in the solution of $ZnCl_2$, $MnCl_2$, $NiCl_2$, $CoCl_2$ of different ionic strengths. The procedure was identical with that previously described except that the solutions of the above mentioned salts were used instead of sodium chloride.

The following combinations were tried:

Merino Wool

(a) Acid titration

(i) No Salt

(ii) Acid + 0.1M salt (Na.Cl)

(iii) Acid + 1.0M salt (N.Cl)

(b) Alkali titration

(i) Na OH - no salt

(ii) Na OH + 0.1M salt (Na.Cl)

(iii) Na OH + 1.0M salt (Na.Cl)

(c) Divalent cation - Titration

(i) Acid + $\frac{M}{3}$ $ZnCl_2$ (ionic strength: μ = 1.0)

(ii) Acid + $\frac{M}{3}$ $MnCl_2$ (ionic strength: μ = 1.0)

(iii) Acid + $\frac{M}{3}$ $NiCl_2$ (ionic strength: μ = 1.0)

(iv) Adic + $\frac{M}{3}$ $CoCl_2$ (ionic strength: μ = 1.0)

(v) Acid + $\frac{M}{30}$ $ZnCl_2$ (ionic strength: μ = 0.1)

(vi) Acid + $\frac{M}{30}$ $MnCl_2$ (ionic strength: μ = 0.1)

(vii) Acid + $\frac{M}{30}$ $CoCl_2$ (ionic strength: μ = 0.1)

(d) Divalent Cation - Titration - (in Alkali)

(i) NaOH + $\frac{M}{3}$ $ZnCl_2$ (Ionic strength: μ = 1.0)

(ii) NaOH + $\frac{M}{3}$ $MnCl_2$ (Ionic strength: μ = 1.0)

(iii) NaOH + $\frac{M}{3}$ $NiCl_2$ (Ionic strength: μ = 1.0)

(iv) NaOH + $\frac{M}{3}$ $CoCl_2$ (Ionic strength: μ = 1.0)

Cross Wool

(a) Acid Titration

(i) No salt + HCl

(ii) Acid HCl + 0.1M NaCl

(iii) Acid HCl + 1.0M NACl

(b) Alkali Titration

(i) NaOH No salt

(ii) NaOH + 0.1M NaCl

(iii) NaOH + 1.0M NaCl

(c) (c) Divalent cation in presence of Acid-Titration

(i) Acid HCl + $\frac{M}{3}$ $ZnCl_2$ (Ionic strength: μ = 1.0)

(ii) Acid HCl + $\frac{M}{3}$ $MnCl_2$ (Ionic strength: μ = 1.0)

(iii) Acid HCl + $\frac{M}{3}$ $NiCl_2$ (Ionic strength: μ = 1.0)

(iv) Acid HCl + $\frac{M}{3}$ $CoCl_2$ (Ionic strength: μ = 1.0)

Yankas Wool

(a) Acid Titration

(i) HCl - No salt

(ii) Acid HCl + 0.1M NaCl

(iii) Acid HCl + 1.0M NaCl

(b) Alkali Titration

(i) NaOH + No salt

(ii) NaOH + 0.1M NaCl

(iii) NaOH + 1.0M NaCl

(c) Divalent Cation in presence of Acid- Titration

(i) Acid HCl + $\frac{M}{3}$ $ZnCl_2$ (Ionic strenght: μ = 1.0)

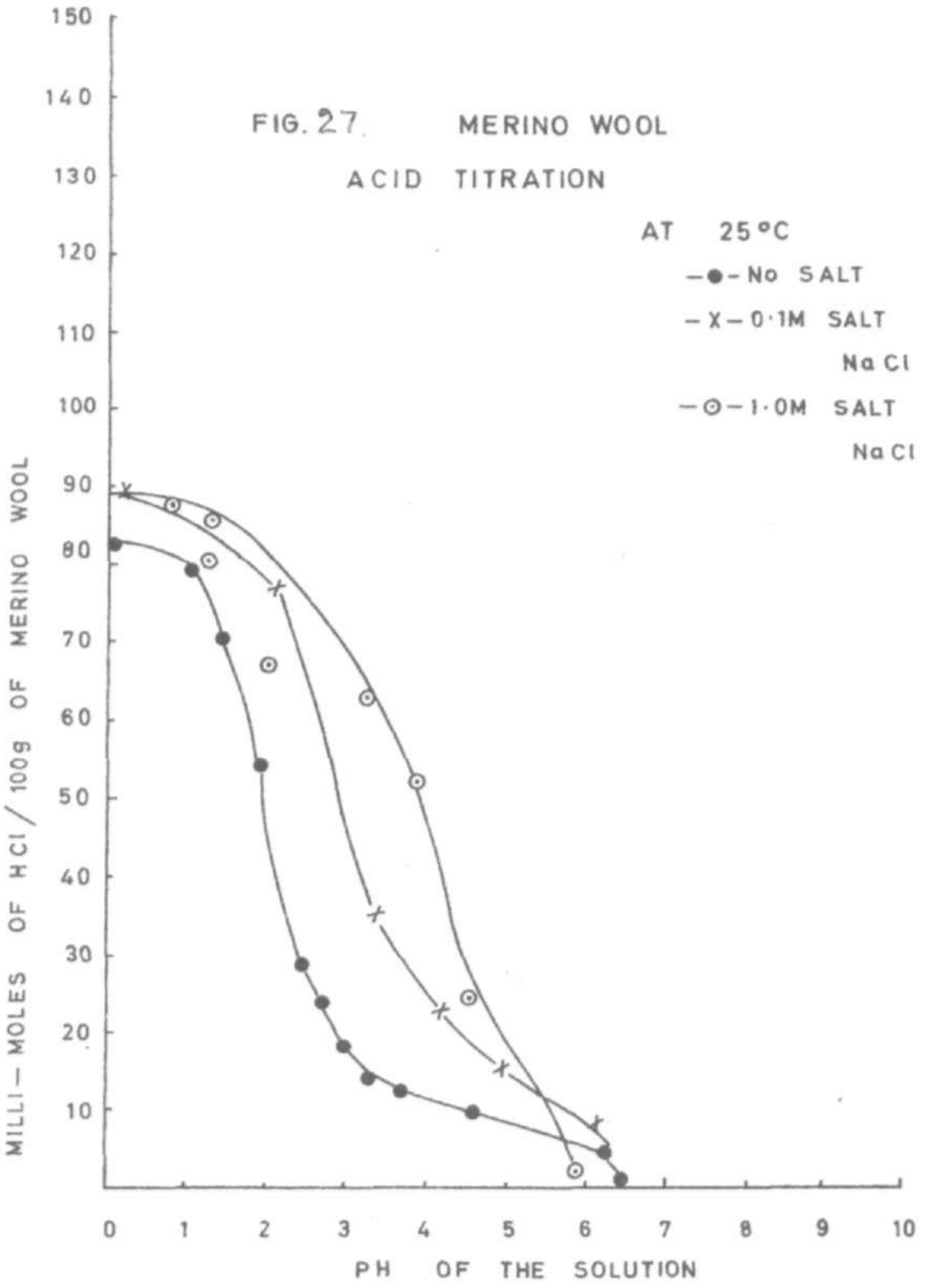
(ii) Acid HCl + $\frac{M}{3}$ $MnCl_2$ (Ionic strenght: μ = 1.0)

(iii) Acid HCl + $\frac{M}{3}$ $NiCl_2$ (Ionic strenght: μ = 1.0)

(iv) Acid HCl + $\frac{M}{3}$ $CoCl_2$ (Ionic strenght: μ = 1.0)

FIG. 27 MERINO WOOL

ACID TITRATION



GRAPH.28 ·(CURVE)

CROSS WOOL

ACID TITRATION

AT 25°C

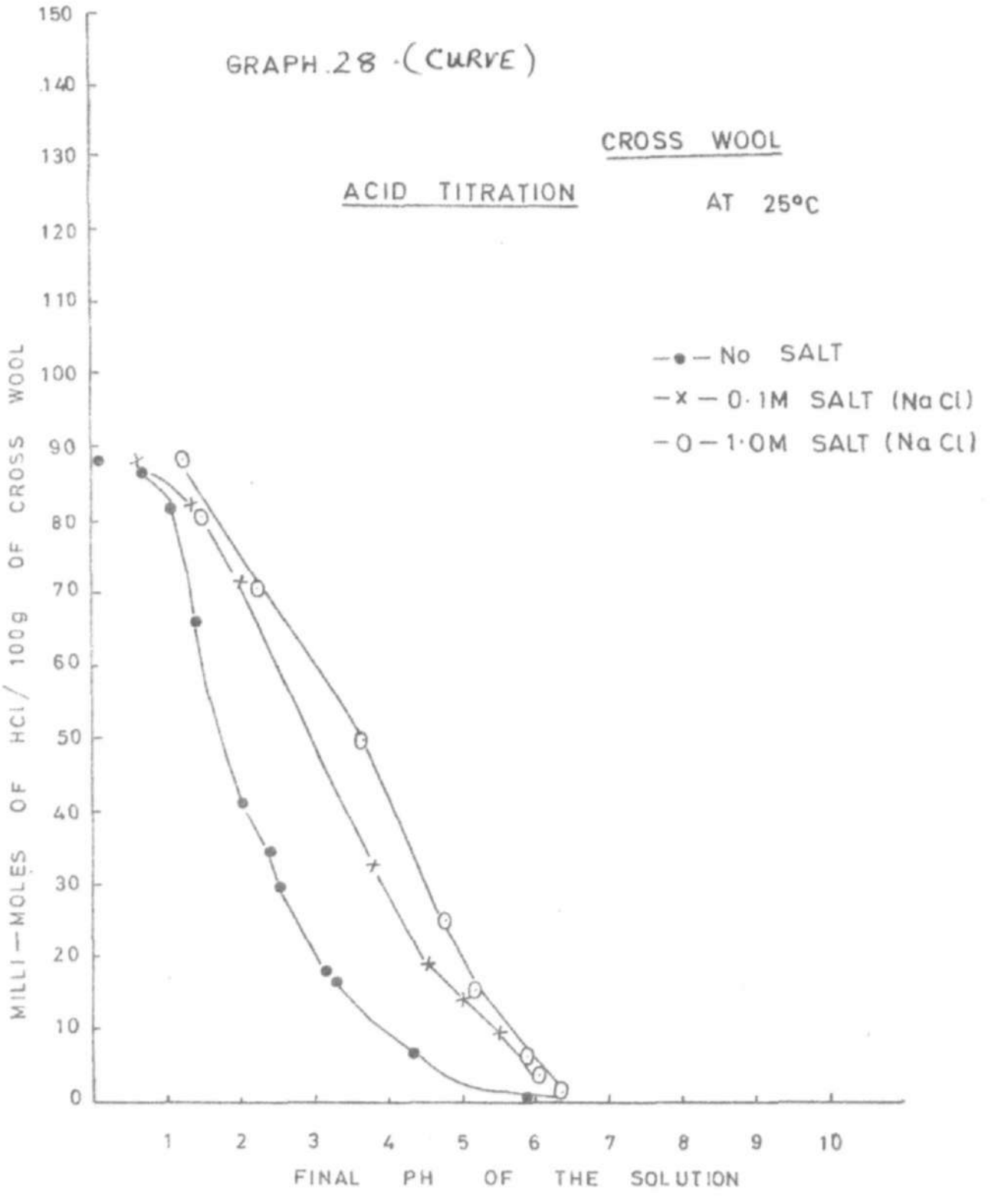
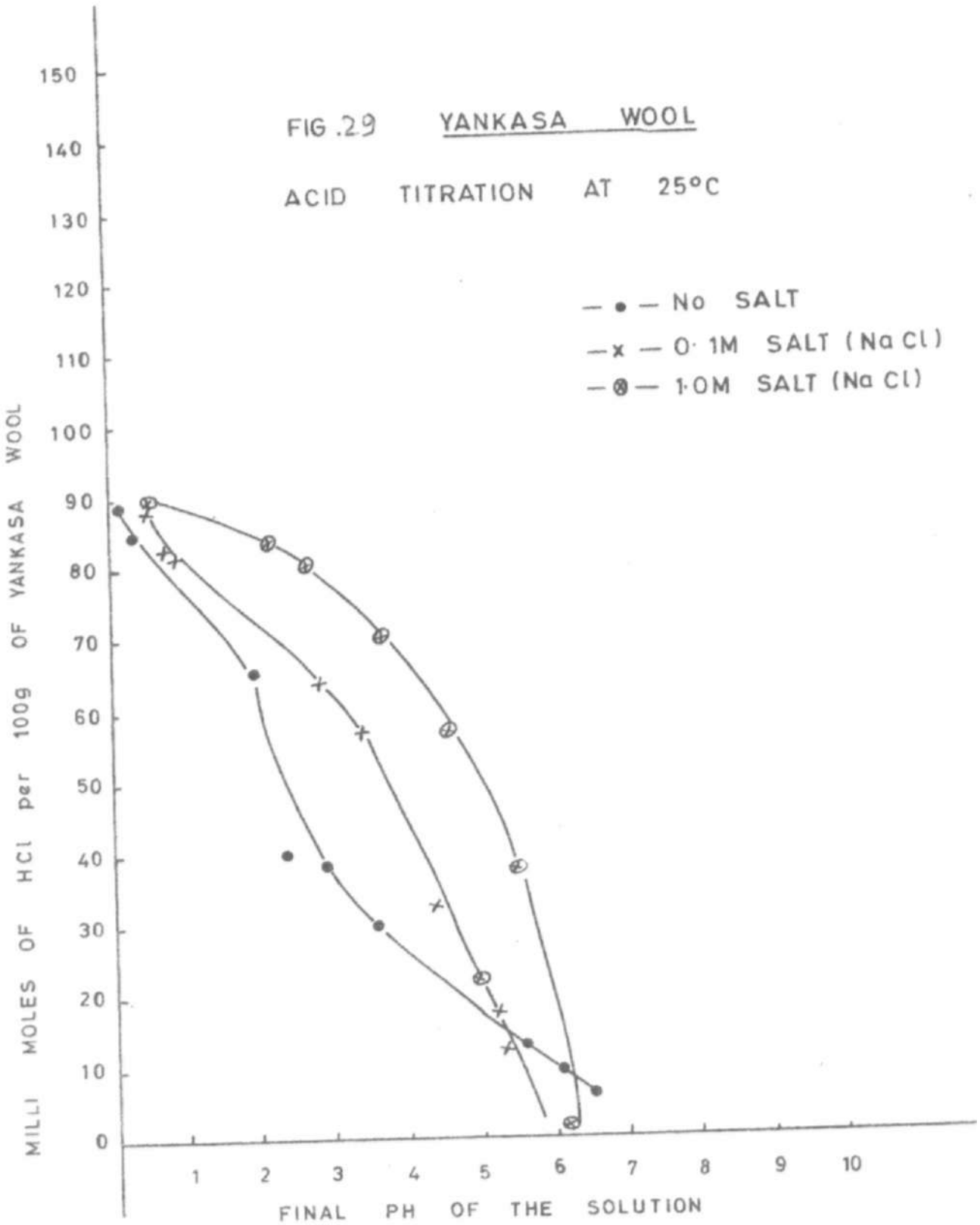


FIG .29 YANKASA WOOL

ACID TITRATION AT 25°C



5.3.0 Results and Discussion

The experimental data obtained for the titration of different wools are reported in the Tables 1 to 38 in the appendix and graphs are plotted (vide Fig. 5.1). These data are obtained for three different sorts of wool (Merino, Cross and Yankasa). 5.3 2
The effect of salt concentrations (NaCl) on the acid-base titration curves for wool are also obtained and illustrated in figures 30, 31, 32. The results of acid titration in the presence of metallic ions are separately discussed.

5.3.1 Characteristics of acid-base titration curves:

The acid titration equation for a wool given by Mathieson and Whewell (50) is used to calculate the pK'_o at various ionic strengths. To calculate the net concentration of fixed charges, the swelling of the wool has to be taken into account. As there is little effect of theacid on the degree of swelling, the swelling in water is used throughout the calculation, together with the density of wool.

The equation for the titration is:

$$pH = pK'_o - \log\left(\frac{1-\alpha}{\alpha}\right) - \frac{0.4343}{RT}\left[\Psi_F + \Pi\bar{V}_H - \Delta\mu_H^o\right] \quad \ldots\ldots\ldots\ldots (35)$$

Where pK'_o is the intrinsic dissociation constant of the titrating groups in the fibre, α is the degree of dissociation, Ψ is the electrostatic potential of the fibre, Π the osmotic pressure,

$\bar{V}_H$ the partial molar volume of the hydrogen ion, and $\Delta\mu_H^o$ the difference of standard chemical potential in the fibre and the solution.

In case of the hydrochloric acid titration of wool, the osmotic pressure, and difference of standard chemical potential in the fibre and the solution may be neglected as the fibre is uniform throughout. The equation by Hartley and Roe (51) is most appropriate for calculation or pK'_o. Their equation is:

$$pH = pK'_o - \log \frac{(1-\alpha)}{\alpha} + (0.4343 \gamma\psi/RT)$$

The modified equation which is more simple and in the presence of salt added, following relationship is more useful.

$$pH = pK'_o - \log \frac{(1-\alpha)}{\alpha} - \frac{0.4343}{RT} \sinh^{-1} (C/2C_s)$$

where α is the degree of dissociation, $C = 0.90\ (1-\alpha)\ 1.4 \times \frac{140}{168}$ the term 1.4 is taken as the density of dry wool, $\frac{140}{168}$ is swelling factor correction, C_s = ionic strength ($\mu = 0.1$ then $C_s = 0.1$)

The above equation is applied to calculate the pK'_o where

$$pK'_o = pH + \log \frac{1-\alpha}{\alpha} + 0.4343 \sinh^{-1} (C/2C_s)$$

In order to caculate the pK'_o in the presence of M^{2+} the values of metal ions are to be also included.

Hence, pK'_o in this case is $pK'_o = pH + \log \frac{1-\alpha}{\alpha} + 0.4343 \sinh^{-1} (C/4C_s)$

The Table for pK'_o values for acid titration is given on page 157

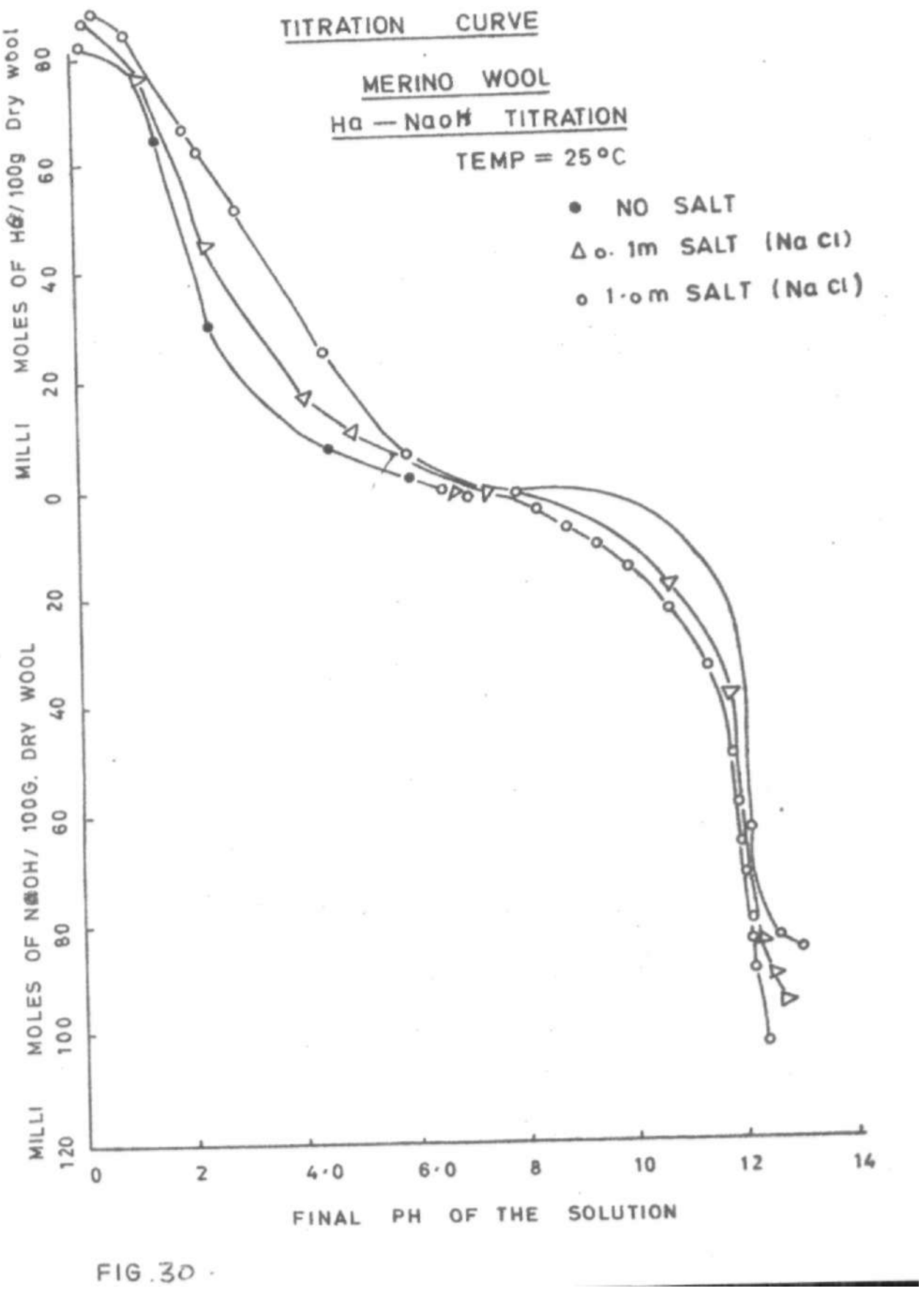

TITRATION CURVE
MERINO WOOL
Ha — NaoH TITRATION
TEMP = 25°C
• NO SALT
Δ o. 1m SALT (Na Cl)
o 1·o m SALT (Na Cl)
MILLI MOLES OF HCl/ 100g Dry wool
MILLI MOLES OF NaOH/ 100G. DRY WOOL
0 20 40 60 80 0 20 40 60 80 100 120
0 2 4·0 6·0 8 10 12 14
FINAL PH OF THE SOLUTION

FIG. 30 .

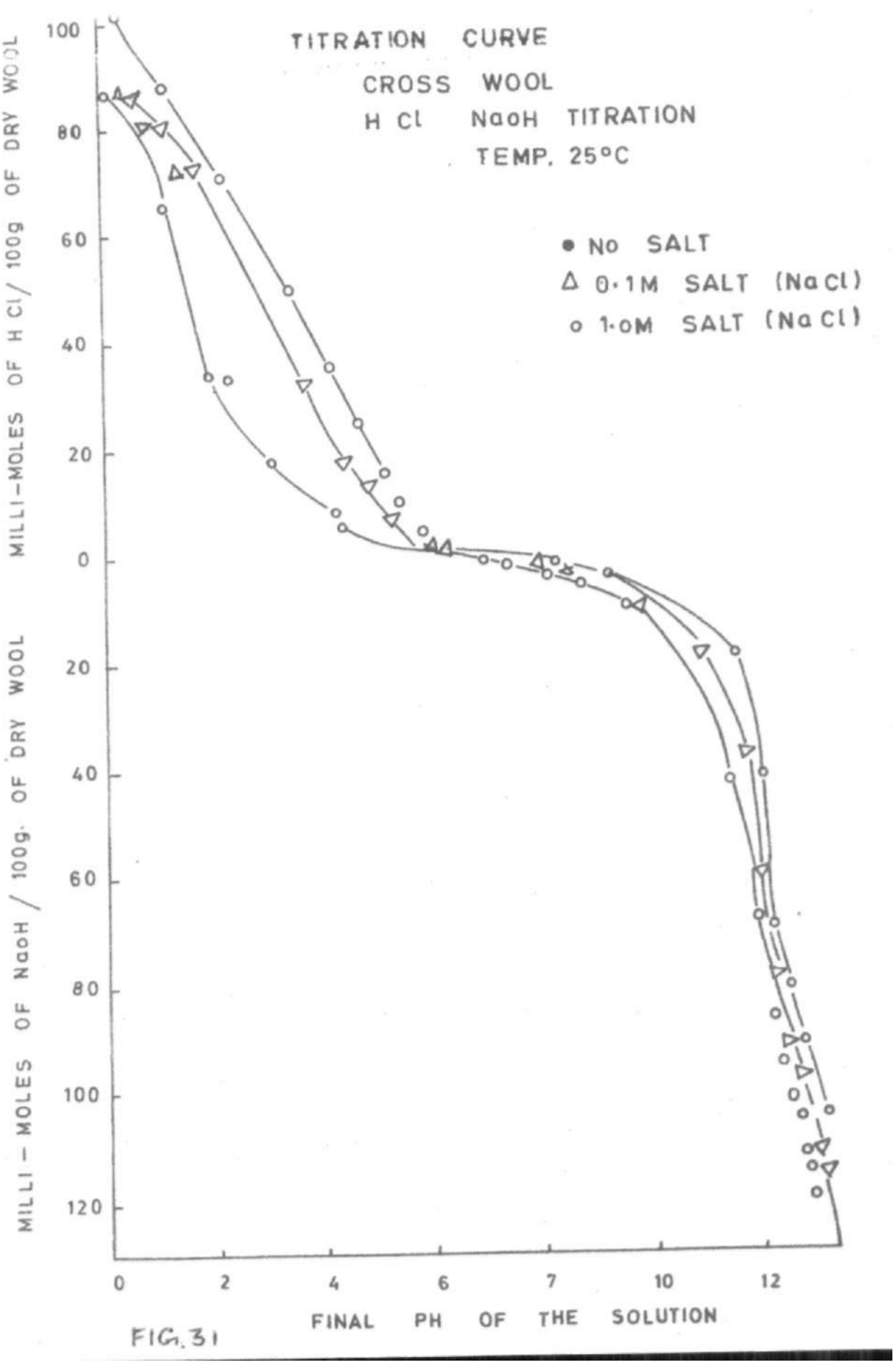

TITRATION CURVE
CROSS WOOL
H Cl NaoH TITRATION
TEMP. 25°C
• No SALT
Δ 0·1M SALT (NaCl)
o 1·0M SALT (NaCl)
MILLI-MOLES OF H Cl/ 100g OF DRY WOOL
MILLI - MOLES OF NaoH / 100g. OF DRY WOOL
100
80
60
40
20
0
20
40
60
80
100
120
0
2
4
6
7
10
12
FINAL PH OF THE SOLUTION

FIG. 31

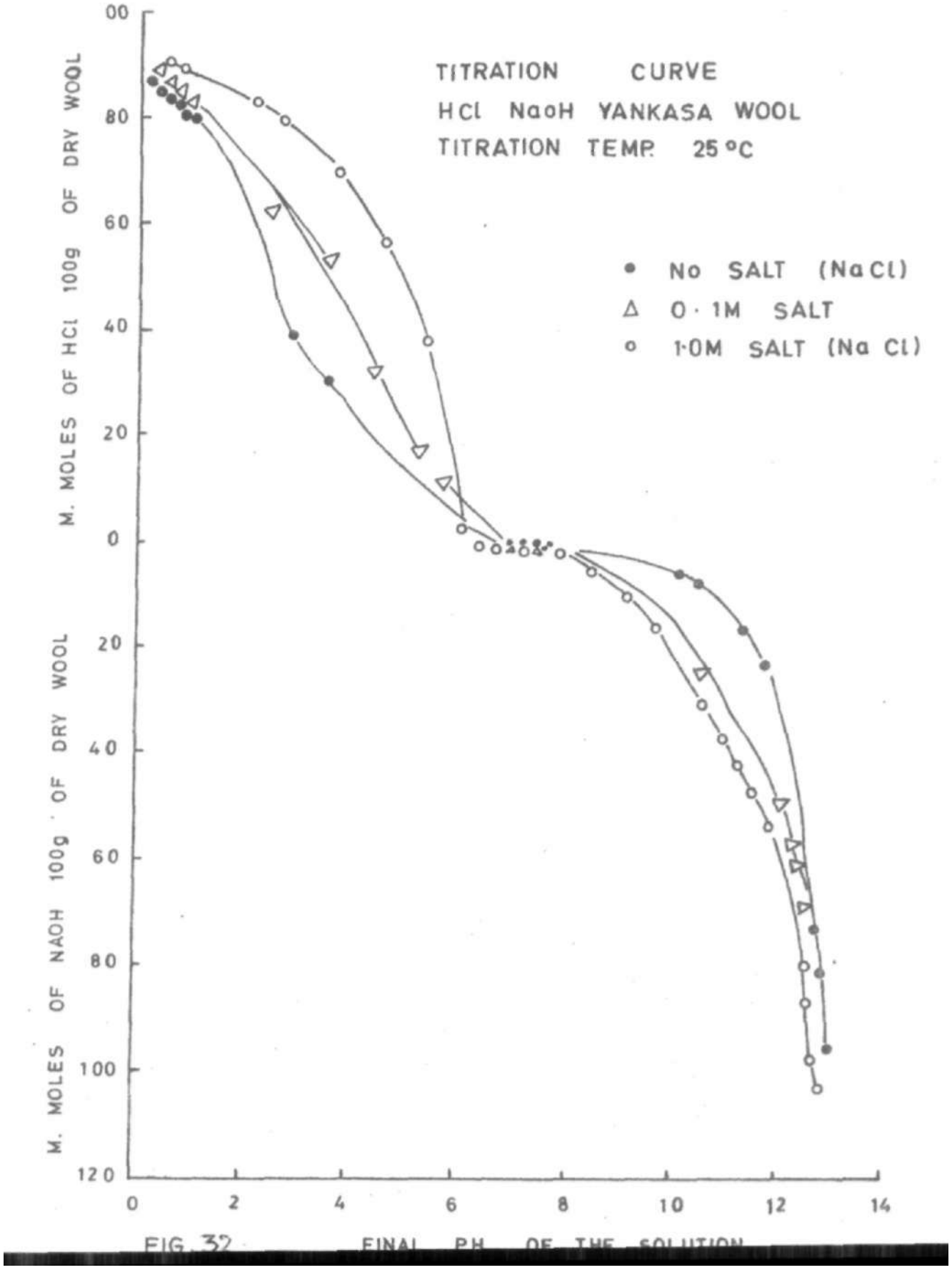

TITRATION CURVE
HCl NaoH YANKASA WOOL
TITRATION TEMP. 25 °C
No SALT (NaCl)
0·1M SALT
1·0M SALT (Na Cl)
M. MOLES OF HCl 100g OF DRY WOOL
M. MOLES OF NAOH 100g OF DRY WOOL
00
80
60
40
20
0
20
40
60
80
100
120
0
2
4
6
8
10
12
14
FINAL PH OF THE SOLUTION

FIG. 32

TABLE NO. 5.4

MERINO WOOL NO SALT ADDED, HCl. $C = 1.05\ (1 - \alpha)$

pH_2	$1-\alpha$	C	C_s(HCl)	$C/2C_s$	0.4343 $\sinh^{-1} C/2C_s$	pK_o
4.25	0.1	0.105	5.62×10^{-5}	930	-	6.27
3.15	0.2	0.210	7.08×10^{-4}	149	2.46	4.7
2.55	0.3	0.315	2.82×10^{-3}	56	2.05	4.23
2.30	0.4	0.420	5.01×10^{-3}	42	1.92	4.04
2.05	0.5	0.525	8.91×10^{-3}	29	1.76	3.81
1.80	0.6	0.630	1.59×10^{-2}	20	1.60	3.58
1.65	0.7	0.735	2.24×10^{-2}	16.4	1.52	3.54
1.35	0.8	0.840	4.47×10^{-2}	9.42	1.28	3.24
0.9	0.9	0.945	1.26×10^{-1}	3.80	0.89	2.74

TABLE NO. 5.5 CROSS WOOL, NO SALT ADDED, $C = 1.05\ (1 - \alpha)$

4.50	0.1	0.105	1.00×10^{-4}	525	3.02	6.07
3.10	0.2	0.210	7.94×10^{-4}	132	2.42	4.91
2.45	0.3	0.315	3.55×10^{-3}	44.3	1.95	4.03
2.00	0.4	0.420	1.00×10^{-2}	21.0	1.63	3.45
1.70	0.5	0.525	2.00×10^{-2}	13.1	1.42	3.12
1.45	0.6	0.630	3.55×10^{-2}	8.9	1.25	2.88
1.30	0.7	0.735	5.01×10^{-2}	7.4	1.17	2.84
1.20	0.8	0.840	6.31×10^{-2}	6.7	1.13	2.84
0.90	0.9	0.945	1.26×10^{-1}	3.8	0.89	2.74

VALUES OF pK_o FOR CROSS WOOL AT TEMP. 25°C

NO SALT ADDED.

TABLE NO. 5.6 YANKASA WOOL NO SAIT C = 1.05 $(1 - \alpha)$

pH_2	$(1 - \alpha)$	C	C_s(HCl)	$C/2C_s$	0.4343 si.nh^{-1} $c/2C_s$	pK_o
5.45	0.1	0.105	3.50×10^{-6}	15000	4.48	8.98
4.60	0.2	0.210	2.51×10^{-5}	4180	3.92	7.91
3.75	0.3	0.315	1.78×10^{-4}	885	3.25	6.63
3.05	0.4	0.420	8.91×10^{-4}	236	2.67	5.54
2.65	0.5	0.525	2.24×10^{-3}	117	2.37	5.02
2.35	0.6	0.630	4.47×10^{-3}	70.5	2.15	4.63
2.05	0.7	0.735	8.71×10^{-3}	41.0	1.91	4.33
1.65	0.8	0.840	2.24×10^{-2}	13.7	1.57	3.33
1.00	0.9	0.945	1.00×10^{-1}	4.72	0.98	2.93

VALUES OF pK_o FOR YANKASA WOOL AT TEMP = 25°C

NO SAIT ADDED.

5.7

TABLE NO. VALUES OF pK_o FOR MERINO WOOL AT TEMP. 25°C
IN PRESENCE OF 0.1M NaCl

MERINO WOOL

C_s = 0.1

pH_2	1-α	C	$C/2C_s$	0.4343 $\sinh^{-1}$ $C/2C_s$	pK_o
5.25	0.1	0.105	0.525	0.22	4.52
4.10	0.2	0.280	1.05	0.4	3.89
3.35	0.3	0.315	1.58	0154	3.52
2.80	0.4	0.420	2.10	0.65	3.27
2.30	0.5	0.525	2.63	0.73	3.03
2.05	0.6	0.630	3.15	0.81	3.04
1.70	0.7	0.735	3.68	0.87	2.99
1.50	0.8	0.840	4.20	0.93	3.04
1.00	0.9	0.945	4.73	0.98	2.94

TABLE NO. 5.8 VALUES OF pK_o FORM MERINO WOOL

MERINO WOOL, 1.0M NaCl. IN PRESENCE OF 1.0M NaCl

5.65	0.1	0.105	0.053	0.02	4.72
5.00	0.2	0.210	0.105	0.05	4.44
4.35	0.3	0.315	0.158	0.07	4.05
3.80	0.4	0.420	0.210	0.09	3.61
3.30	0.5	0.525	0.263	0.11	3.41
2.75	0.6	0.630	0.315	0.13	3.06
2.20	0.7	0.735	0.368	0.16	2.73
1.75	0.8	0.840	0.420	0.18	2.54
1.15	0.9	0.945	0.473	0.20	2.35

TABLE NO. 5.9 VALUES OF pK_o FOR CROSS WOOL AT TEMP = 25°C

CROSS WOOL IN PRESENCE OF 1.0 N NaCl

pH_2	$1-\alpha$	C	$C/2C_s$	$0.4343 \sinh^{-1} C/2C_s$	$\frac{\text{Log } 1-\alpha}{\alpha}$	pK_o
5.45	0.1	0.105	0.057	0.02	-0.95	4.52
4.95	0.2	0.210	0.105	0.05	-0.61	4.39
4.55	0.3	0.315	0.158	0.07	- .37	4.25
4.10	0.4	0.420	0.210	0.09	-0.18	4.01
3.65	0.5	0.525	0.263	0.11	0.0	3.76
3.25	0.6	0.630	0.315	0.13	+0.18	3.56
2.75	0.7	0.735	0,365	0.16	+0.37	3.28
2.05	0.8	0.840	0.420	0.18	+0.61	2.84
1.65	0.9	0.945	0.473	0.20	+0.95	2.80

TABLE No. 5.10

CROSS WOOL, 0.1 M NaCl, $C = 1.05 (1-\alpha)$

5.15	0.1	0.105	0.22	-0.95	4.42
4.40	0.2	0.210	0.4	-0.61	4.19
4.00	0.3	0.315	0.54	-0.37	4.17
3.60	0.4	0.420	0.65	-0.18	4.07
3.10	0.5	0.525	0.73	-00.0	3.83
2.65	0.6	0.630	0.81	+0.18	3.64
2.25	0.7	0.735	0.87	+0.37	3.49
1.85	0.8	0.840	0.93	+0.61	3.39
1.25	0.9	0.949	0.98	+0.95	3.80

TABLE NO. 5.11 YANKASA WOOL. 1.0 M NaCl $C = 1.05 (1 - \alpha)$

VALUES OF pK_o FOR YANKASA WOOL AT TEMP = 25°C

pH_2	$1 - \alpha$	C	0.4343 $\sinh^{-1} C/2C_s$	pK_o
6.05	0.1	0.105	0.02	5.12
5.85	0.2	0.210	0.05	5.29
5.65	0.3	0.315	0.07	5.35
5.45	0.4	0.420	0.9	5.36
5.15	0.5	0.525	0.11	5.26
4.70	0.6	0.630	0.13	5.01
4.25	0.7	0.735	0.16	4.78
3.55	0.8	0.840	0.18	4.34
2.55	0.9	0.945	0.20	3.70
1.75	0.95		0.21	3.22

TABLE NO.5.12 VALUES OF pK_o FOR YANKASA WOOL AT TEMP. 25°C IN PRESENCE OF 0.1 M NaCl.

5.90	0.1	0.105	0.22	5.17
5.30	0.2	0.210	0.40	5.09
4.70	0.3	0.315	0.54	4.87
4.30	0.4	0.420	0.65	4.77
3.80	0.5	0.525	0.73	4.53
3.25	0.6	0.630	0.81	4.24
2.75	0.7	0.735	0.87	3.99
2.10	0.8	0.840	0.93	3.64
1.25	0.9	0.945	0.98	3.18
0.75	0.95	1.00	1000	3.01

Table No. 5. 13.

pK'_o Values for Acid Titration of Wools ($25^{\circ}C$)

1-α	YANKASA				MIXED BRED				MERINO				AVR MIXED AND MERINO
	No. Salt	0.1M	1.0M	AV	No. Salt	0.1M	1.0M	AV	No. Salt	0.1M	1.0M		
0.1	-	5.17	5.12	5.14	-	4.42	4.52	4.47	-	4.52	4.82	4.62	4.55
0.2	--	5.09	5.29	5.19	4.91	4.19	4.39	4.50	5.00	3.94	4.44	4.46	4.49
03	-	4.87	5.35	5.22	4.03	4.17	4.25	4.15	4.23	3.77	4.05	4.02	4.09
04	-	4.77	5.36	5.13	3.45	4.07	4.01	3.84	4.04	3.57	3.61	3.74	3.79
05	5.02	4.53	5.26	4.94	3.12	3.83	3.76	3.57	3.82	3.33	3.41	3.52	3.55
06	4.68	4.24	5.01	4.64	2.88	3.64	3.56	3.39	3.59	3.19	3.06	3.28	3.34
07	4.33	3.99	4.78	4.37	2.84	3.49	3.28	3.21	3.54	3.09	2.73	3.12	3.17
08	3.83	3.64	4.34	3.94	2.84	3.39	2884	3.02	3.24	2.79	2.54	2.89	2.96
0.9	2.93	3.18	3.70	3.27	2.74	3.18	2.80	2.91	2.74	2.64	2.30	2.56	2.74
0.95	-	3.01	3.22	3.12	-	-	-	-	-				

5.3.2 pK'_o values for the acid titration of wool:

The results given in the table 1-37 for the titration of three varieties of wool by HCl in the presence of sodium chloride are interpreted by the theory put forward by Mathieson and Whewell (50). Some comments to explain the behavior of these wools are given below.

The results show that pK'_o is reasonably independent of ionic strength within experimental error.

pK'_o falls as $(1-\alpha)$ rises for all the wools. The pK'_o values for the different wools are relatively close to each other. This agrees with their similarity in amino acid composition (vide chapter 2) and structure, especially for Merino and Cross wools. A simple equation describing the relationship between pK'_o and $(1-\alpha)$ has been established for Merino and Cross wools:

$$pK'_o = 4.8 - 2.6\ (1-\alpha) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (37)$$

The Yankasa wool behaves differently. When the relation of pK'_o to $(1-\alpha)$ is found for the results for Yankasa wool, it is found that pK'_o varies between the same limits as for the other wools, i.e. (4.8 to 2.6) but not linearly. In the beginning, as $(1-\alpha)$ increases, the pK'_o values remains approximately constant up to about $1-\alpha = 0.5$, then they fall smoothly till they reach the minimum value of 2.6.

The maximum acid combining capacity obtained by titration for different types of wool are given in the Table 5.14. Consistency is shown in the acid up take by HCl. They have 89.3 - 90.0 milli-moles per 100g of titrable acid groups. These results are in accordance with the results given by different workers (Steinhard and Harris. (17)

When titration proceeds from neutrality, wool titrates preferably $-COO^-$ groups not salt linked to the basic groups.

Merino behaves similarly to the Cross wool, so they have equal numbers of salt-linked and non-linked groups like Lincoln wool (50). The maximum value of pK'_o is considered to be $pK'_p = 4.8$ and minimum value (2.6) is pK'_q. It is noted that pK'_q of the salt linked groups of the wool is lower (2.6) as against 3.3 (25°C) for Lincoln wool. The pK_p and pK_q for Lincoln wool at different temperature are given below (56).

Lincoln Wool

Temperature °C	pK'_p	pK'_q
0	4.855	3.585
25	4.95	3.33
30	5.06	3.24

It seems that the salt-link is stronger and the groups are perhaps closer together in Merino and Cross than in Lincoln wool.

Initially, Yankasa wool titrates only non-salt linked $-COO^-$ groups. These are nearly half of the total groups which are titrable. Thereafter, both salt-linked and non salt-linked groups are titrated, but less than one quater of the total are salt-linked.

It is also noted that Yankasa wool has a bigger affinity towards acid as compared to the Merino and Cross.

The titration curves for alkali without added salt (vide Figure 30, 31, 32) are in the order of Yankasa wool > Merino > Cross up to 11.5 pH. Below 11.5 pH for the ionic strength of 1.0M and 0.1 (NaCl), the order is Cross > Yankasa wool > Merino. Above pH 11.5, the order of the titration curves is Cross = Merino > Yankasa Wools for all the ionic strength and for no salt present. There is not much difference in the behavior of these wools in the alkaline titration. Up to 11.5 pH, perhaps about the same number of ionisible groups are titrated and perhaps the same factors operate.

Above pH 11.5, hydrolysis may be effective (due to high concentration of alkali) which may be responsible for the different behavior of these wools. It is also noted from the titration data that below pH 11.5, histidine, lysine and terminal amino groups are titrated. Above pH 11.5, the titrable groups are those of tyrosine, arginine and hydrolysis products. The intersection of the alkaline titration curves at about 11.5 pH suggests that about the same number of lysine, histidine and terminal amino groups are present in the three wools, but perhaps titrate more easily in Yankasa wool.

Table No. 5.14

Maximum Combining Capacity of HCl By Different Wools.

milli-moles of HCl/100g of wool at Temp. 25°C

In presence of	Merino		Cross		Yankasa	
	μ = 1.0	μ = 0.1	μ = 1.0	μ = 0.1	μ = 1.0	μ = 0.1
No salt	83.3	-	88.2	-	89.3	-
NaCl	89.3	89.3	88.2	88.2	89.3	90.2
$CoCl_2$	120.0	95.0	112.0	-	160.0	-
$ZnCl_2$	104.0	120.0	102.0	-	108.0	-
$NiCl_2$	130.0	95.0	138.0	-	150.0	-
$MnCl_2$	122.0	100.0	125.0	-	104.0	-

5.3.3 Interpretation of Acid Titration in Terms of Amino Acid Composition (in Presence of NaCl Only)

Table No.5.15.

The Total Amino Acid (Basic) M: Moles/100g of Wool

Amino Acid	Merion	Cross	Yankasa
ARG.	62.5	57.0	59.7
LYS	25.3	24.0	29.1
HIS.	6.1	5.9	5.9
TOTAL	93.9	86.9	94.7

As previously stated, the same amount of acid is taken up ($86 \simeq 94$), due to the presence of charged lysine, histidine and arginine groups. There seem to be no effect due different ionic strength. The acid uptake is approximately constant ($\simeq 90$).

If calculation is made on the basis of the amount of acid required for titration of the acidic side chains of wool which are ionized at neutrality, from the amino acid composition of the different wool, the theoretical acid-binding capacity of the wool is from 86.9 - 94.7 milli-moles/100g.

Hence reasonable agreement is found between the calculated values of these groups from the titration data and the amino acid composition; but there are more acid groups already there as - COOH or $-CONH_2$ as shown by the content of glutamic and aspartic acid

(see the table). In presence of divalent metal ion some or all of these -COOH groups will have become $-COO^{-}M^{2+}$ at neutrality and so be available for titration by HCl, thus increasing the maximum acid combining capacity above 90 m. moles per 100g in the presence of the metal ion. This clearly demonstates that divalent metal ions do bind to carboxyl groups and exchange with hydrogen ion in the process.

5.3.4 Interpretation of Acid Titration in the Light of Acid Titration Theories:

The theory of Mathieson and Whewell (50) is the extension of the theory for the soluble polyelectrolytes. This theory considers that the electrostatic potential ψ is the key term in the titration equation. The complete equation for polyelectrolyte fibre is already given earlier on page 134 When the theory was applied to Lincoln wool, $(1-\alpha)$ was plotted against pK'_o, a straight line was obtained. The results of the titration of Merino and Cross wools show that pK'_o varies with $1-\alpha$ linearly, but is independent of ionic strength. This indicates that the theory is obeyed and the osmotic term is negligible. The relation between the pK'_o and $1-\alpha$ has already been given. The pK'_p of Merino will be 4.8 and pK'_q for the same wool will be 2.6.

So far as Yankasa wool is considered, its behavior is slightly different

TABLE NO 5.16

VALUES OF pK_o for MERINO WOOL AT TEMPERATURE 25°C

IN PRESENCE OF 0.33 M $ZnCl_2$) C_s = 0.33

pH_2	$1-\alpha$	C	0.4343 $\sinh^{-1} C/4C_s$	pK_o
4.20	0.1	0.105	0.03	3.28
3.95	0.2	0.210	0.07	3.41
3.73	0.3	0.315	0.10	3.41
3.48	0.4	0.420	0.14	3.44
3.25	0.5	0.525	0.17	3.411
3.03	0.6	0.630	0.20	3.471
2.78	0.7	0.735	0.23	3.38
2.53	0.8	0.840	0.26	3.40
1.98	0.9	0.945	0.29	3.22
5.17	MERINO WOOL	(0·33 M $MnCl_2$)	$C_s = 0·33$	
4.80	0.1	0.05	0.03	3.88
4.3	0.2	0.210	0.07	3.59
3.45	0.3	0.315	0.10	3.18
2.77	0.4	0.420	0.14	2.73
2.50	0.5	0.525	0.17	2.67
2.35	0.6	0.630	0.20	2.63
2.22	0.7	0.735	0.23	2.82
2.09	0.8	0.840	0.26	2.96
1.02	0.9	0.945	0.29	3.16

TABLE NO. 5.18

VALUES OF pK_o FOR MERINO WOOL AT TEMPERATURE 25°C

IN PRESENCE OF 0.33 M $NiCl_2$ SOLUTION

$C_s = 0.33$

pH_2	$1-\alpha$	C	0.4343 $\sinh^{-1} c/4C_s$	pK_o
5.30	0.1	0.105	0.03	4.38
4.90	0.2	0.210	0.07	4.36
4.50	0.3	0.315	0.10	4.23
4.12	0.4	0.420	0.14	4.08
3.75	0.5	0.525	0.17	3.92
3.37	0.6	0.630	0.20	3.75
2.95	0.7	0.735	0.23	3.55
2.37	0.8	0.840	0.26	3.24
2.11	0.9	0.945	0.29	3.35

TABLE NO. 5.19 MERINO WOOL $CoCl_2$ (0.33 M) At Temp. 25°C

5.2	0.1	0.105	0.03	4.28
4.78	0.2	0.210	0.07	4.24
4.35	0.3	0.315	0.10	4.08
3.95	0.4	0.420	0.14	3.91
3.55	0.5	0.525	0.17	3.72
3.15	0.6	0.630	0.20	3.53
2.62	0.7	0.735	0.23	3.22
2.23	0.8	0.840	0.26	3.10
1.91	0.9	0.945	0.29	3.15

TABLE NO 5.20 VALUES OF pK_o FOR CROSS WOOL AT TEMP. 25°C
IN PRESENCE OF 0.33M $ZnCl_2$ SOLUTION $C_s = 0.33$

pH_2	$1 - \alpha$	C	0.4343 $\sinh^{-1} C/4C_s$	pK_o
4.92	0.1	0.105	0.03	4.00
4.54	0.2	0.210	0.07	4.00
4.28	0.3	0.315	0.10	4.01
4.01	0.4	0.420	0.14	3.97
3.64	0.5	0.525	0.17	3.81
3.02	0.6	0.630	0.20	3.40
2.39	0.7	0.735	0.23	2.99
2.18	0.8	0.840	0.26	3.28
1.90	0.945	0.845	0.29	3.14

TABLE 21 VALUES OF pK FOR CROSS WOOL AT TEMP.25°C
IN PRESENCE OF $CoCl_2$ (0.33M) SOLUTION $C_s = 0.33$

5.12	0.1	0.105	0.03	4.20
4.52	0.2	0.210	0.07	3.98
4.22	0.3	0.315	0.10	3.95
4.06	0.4	0.420	0.14	4.02
3.82	0.5	0.525	0.17	3.99
3.52	0.6	0.630	0.20	3.90
2.77	0.7	0.735	0.23	3.37
2.15	0.8	0.840	0.26	3.02
1.92	0.9	0.945	0.29	3.14

TABLE NO 5.22 VALUES OF pK_o FOR CROSS WOOL AT TEMP. 25°C

IN PRESENCE OF 0.33 M $NiCl_2$ SOLUTION, $C_s = 0.33$

pH_2	$1 - \alpha$	C	$0.4343 \sinh^{-1} C/4C_s$	pK_o
5.18	0.1	0.105	0.03	4.26
4.84	0.2	0.210	0.07	4.30
4.54	0.3	0.315	0.10	4.27
4.23	0.4	0.420	0.14	4.19
4.03	0.5	0.525	0.17	4.20
3.80	0.6	0.620	0.20	4.18
3.57	0.7	0.735	0.23	4.17
3.3	0.8	0.840	0.26	4.17
3.0	0.9	0.945	0.29	4.24

TABLE 5.23. VALUES OF pK_o FOR CORSS WOOL AT TEMP. 25°C

IN PRESENCE OF $MnCl_2$ (0.33M) SOLUTION, $C_s = 0.33$

5.48	0.1	0.105	0.03	4.56
5.14	0.2	0.210	0.07	4.60
4.82	0.3	0.315	0.10	4.55
4.59	0.4	0.420	0.14	4.55
4.32	0.5	0.525	0.17	4.49
4.00	0.6	0.630	0.20	4.38
3.62	0.7	0.735	0.23	4.22
3.16	0.8	0.840	0.26	4.03
2.80	0.9	0.945	0.29	4.04

TABLE NO. 5.24

VALUES OF pK_o YANKASA WOOL AT TEMP. 25 °C

IN PRESENCE OF $ZnCl_2$ (0.33M) C_s = 0.33

pH_2	$1-\alpha$	C	$0.4343 \sinh^{-1} C/4C_s$	pK_o
4.85	0.1	0.105	0.03	3.93
4.30	0.2	0.205	0.07	3.76
4.00	0.3	0.315	0.10	3.73
3.9	0.4	0.420	0.14	3.86
3.70	0.5	0.525	0.17	3.87
3.47	0.6	0.630	0.20	3.85
3.32	0.7	0.735	0.23	3.92
3.02	0.8	0.840	0.26	3.89
2.72	0.9	0.945	0.29	3.96

TABLE NO.5.25 VALUES OF pK_o Yankasa WOOL AT TEMP. 25°C.

IN PRESENCE OF $CoCl_2$ (0.33M) SOLUTION C_s = 0.33

4.82	0.1	0.105	0.03	3.90
4.44	0.2	0.205	0.07	3.90
4.06	0.3	0.315	0.10	3.79
3.70	0.4	0.420	0.14	3.66
3.3	0.5	0.525	0.17	3.47
2.97	0.6	0.630	0.20	3.35
2.62	0.7	0.735	0.23	3.22
2.39	0.8	0.840	0.26	3.26
2.22	0.9	0.945	0.29	3.46

TABLE NO.5.26 VALUES OF pK_o FOR YANKASA WOOL AT TEMP. 25°C IN PRESENCE OF $MnCl_2$ (0.33M) SOLUTION $C_s = 0.33$

pH	1−α	C	0.4343 $\sinh^{-1}$ C/4C_s	pK_o
4.92	0.1	0.105	0.03	4.00
4.78	0.2	0.205	0.07	4.27
4.65	0.3	0.315	0.10	4.38
4.52	0.4	0.420	0.14	4.48
4.40	0.5	0.525	0.17	4.57
4.25	0.6	0.630	0.20	4.63
4.10	0.7	0.735	0.23	4.70
3.92	0.8	0.840	0.26	4.92
3.68	0.9	0.945	0.29	4.92

TABLE NO.5.27 VALUES OF pK_o FOR YANKASA WOOL AT TEMP. 25°C IN PRESENCE OF $MnCl_2$ (0.33M) SOLUTION. $C_s = 0.33$

4.82	0.1	0.105	0.03	3.90
4.64	0.2	0.205	0.07	4.10
4.46	0.3	0.315	0.10	4.27
4.26	0.4	0.420	0.14	4.22
4.03	0.5	0.525	0.17	4.20
3.78	0.6	0.630	0.20	4.16
3.55	0.7	0.735	0.23	4.15
3.29	0.8	0.840	0.26	4.16
2.98	0.9	0.945	0.29	4.22

TABLE 5.28 COMPARISON OF THE ACID UPTAKE BY DIFFERENT WOOLS

Cation	pH of beginning titration		Inflections pH		Inflections m.moles/100 g wool		Max. acid capacity	
	μ = 0.1	μ = 1.0	μ= 0.1	μ= 0.1	μ= 1.0	μ= 1.0	μ= 1.0	μ= 1.0
MERINO: at 25°C								
Na^+	6.5	6.5	0	0	, 90	90	90,	90
Ni^{2+}	5.5	5.6	2.4, 1.0	2.4, 1.4	48, 90	60, 130	95,	130
Co^{2+}	5.6	5.6	1.92, 1.0	2.0, 1.0	52, 110	75, 110	100,	130
Mn^{2+}	5.6	5.6	1.92, 1.0	2.0, 1.0	52, 105	50, 120	105,	120
Zn^{2+}	5.0	4.7	1.42, 1.2	3.6, 2.0	52, 105	10,60,105	120,	100
CROSS WOOL								
Na^+	6.3	6.6	0	0	90	90	90	90
Ni^{2+}	-	5.9	-	1.0	-	138	-,	138
Co^{2+}	-	5.9	-	3.0, 0.8	-	60, 112	-,	112
Mn^{2+}	-	6.5	-	3.0, 1.0	-	60, 125	-,	125
Zn^{2+}	-	5.8	-	3.0, 0.8	-	50, 102	-,	102
LOCAL (YANKASA) WOOL								
Na^+	7.0	6.8	0	0	90	90	90	90
Ni^{2+}	-	5.2	-	1.0	-	150	-,	150
Co^{2+}	-	5.3	-	?, 1.0	-	75, 160	-,	160
Mn^{2+}	-	5.2	-	1.0	-	104	-,	104
Zn^{2+}	-	5.4	-	1.0	-	75, 108	-,	108

TABLE NO. 5.29

MID - POINT OF THE TITRATION (pKa^1) (half titration)

ION	MERINO		CROSS	YANKASA
	1.0 (N)	0.1 (N)	= 1.0 (N)	= 1.0 (N)
Na^+	3.33	2.5	3.7	5.1
Ni^{2+}	4.5, 2.06	3.84, 1.6	3.5	3.8
Co^{2+}	3.8, 1.7	3.6, 1.6	4.3, 1.8	2.2 ?
Mn^{2+}	3.6, 2.0	4.1, 1.6	3.6	3.8
Zn^{2+}	4.2, 3.5, 2	3.8, 1.7	4.3, 2.0	4.9, 3.2

Note:

1. for Na^+, pKa^1 varies Merino < Cross << Local
2. for M^{2+} always two curves (or three for Zn^{2+})
   for Merino; for cross, Mn^{2+}, Ni^{2+} only one curve.
3. for Yankasa, only Zn^{2+} for two curves, rest one curve only.

5.3.5 Metal - Hydrogen Ion-Exchange:

When metal M^{2+} ion is present in the solution, in presence of HCl - the titration may be $H^+ + -COO^-M^{2+} \rightleftharpoons M^{2+} + -COOH$

Applying the law of Mass Action.

$$K_{EX} = \frac{(M^{2+}) \cdot (-COOM)}{(H^+)\ (-COOM^{2+})} \qquad \text{.....(38)}$$

Where $\frac{(-COOM)}{(-COOM^{2+})} = K_{EX}\frac{(H^+)}{(M^{2+})}$

Therefore $\log \frac{(-COOM)}{(COOM^{2+})} = \log K_{EX} + \log (H^+) - \log(M^{2+})$

$= \log K_{EX} - pH - \log M^{2+}$

In order to find the relationship between the pH and log K_{EX}, we may assume,

(a) all $-COO^-$ are present as $-COO^-M^{2+}$ residue

and $\log \frac{(-COOH)}{(COOM)} = \log \frac{(1-\alpha)}{\alpha}$

Hence substituting the value of $\log \frac{(-COOH)}{(COOM)}$ we get

$$\log \frac{(1-\alpha)}{\alpha} = pH + \log K_{EX} - \log M^{2+}$$

$$\text{or } pH + \log\frac{(1-\alpha)}{\alpha} = \log K_{EX} - \log (M^{2+}) \qquad \text{.....(39)}$$

(b) (M^{2+}) is in excess and has the same value inside the fibre as in the external solution, and is consistent,

i.e. $(M^{2+}) = 0.333$ in $\log (M^{2+}) = -0.4770$ (40)

$$\text{Now } pH + \log \frac{(1-\alpha)}{\alpha} + 0.4770 = \log K_{EX} \qquad \text{.....(X)}$$

On these assumptions the equation two can be derived; but meanwhile we are going to ignore.

(i) existence of any more than one metal - carbonyl binding equilibrium, for example, M^{2+} - $(COO^-)_2$ M^{2+} - $(COO^-)_4$, etc.,

(ii) different strengths of binding of M^{2+} to COO^- where some $-COO^-$ are salt-linked and some are not.

(iii) difference of activity coefficient, from unity.

On plotting the curve $(1-\alpha)$ vs log K_{EX} one must expect the linear graph providing all the assumption are true and only one system is in operation.

During the assumption we have also ignored other possible binding equilibria.

Table No. represent the values of log K_{EX} with pH and $(1-\alpha)$ for three wools, at different ionic strengths. The data is obtained on the basis of the equation on page The equation is

$$pH + \log \frac{(1-\alpha)}{\alpha} \cdot 0.477 = \log K_{EX}$$

The graphs obtained on plotting the value of $(1-\alpha)$ verses log K_{EX} can be seen on page

If two curves are obtained then this may be some other type of M^{2+} exchange going on like: $-(COO^-)_2.M^{2+}$ or $-(COO^-)_4.M^{2+}$

For the systems with one curve only, it is possible, though not conclusive, that there is only one M^{2+} - COO^- binding $\rightleftharpoons$ M. One should expect constant values of log K_{EX}. If a constant log K_{EX} is obtained for them over a reasonable range of $(1-\alpha)$, this will be fruitful and will support the assumptions which have already been made - for a system where there are two curves one is bound to get values of log K_{EX} which vary with $(1-\alpha)$.

If large values of K_{EX} or log K_{EX} are obtained it means strong metal ion binding is in operation.

If at $(1-\alpha) = 1$ the value of K_{EX} is smaller than at $(1-\alpha) = 0$, then there may be another unknown factor operating provided some other types of metal exhange.

If there is no specific binding, there should be linear relationship between log K_{EX} and $(1-\alpha)$, This is only true for Na^+ for cross and Merino but not Yankasa.

The dissociation of acid groups can be represented $-COO^- + H^+ \rightleftharpoons -COOH$. Where the dissociation constant for the acid group

$$K = \frac{[COO^-] \cdot [H^+]}{[COOH]} \qquad \text{.....(1)}$$

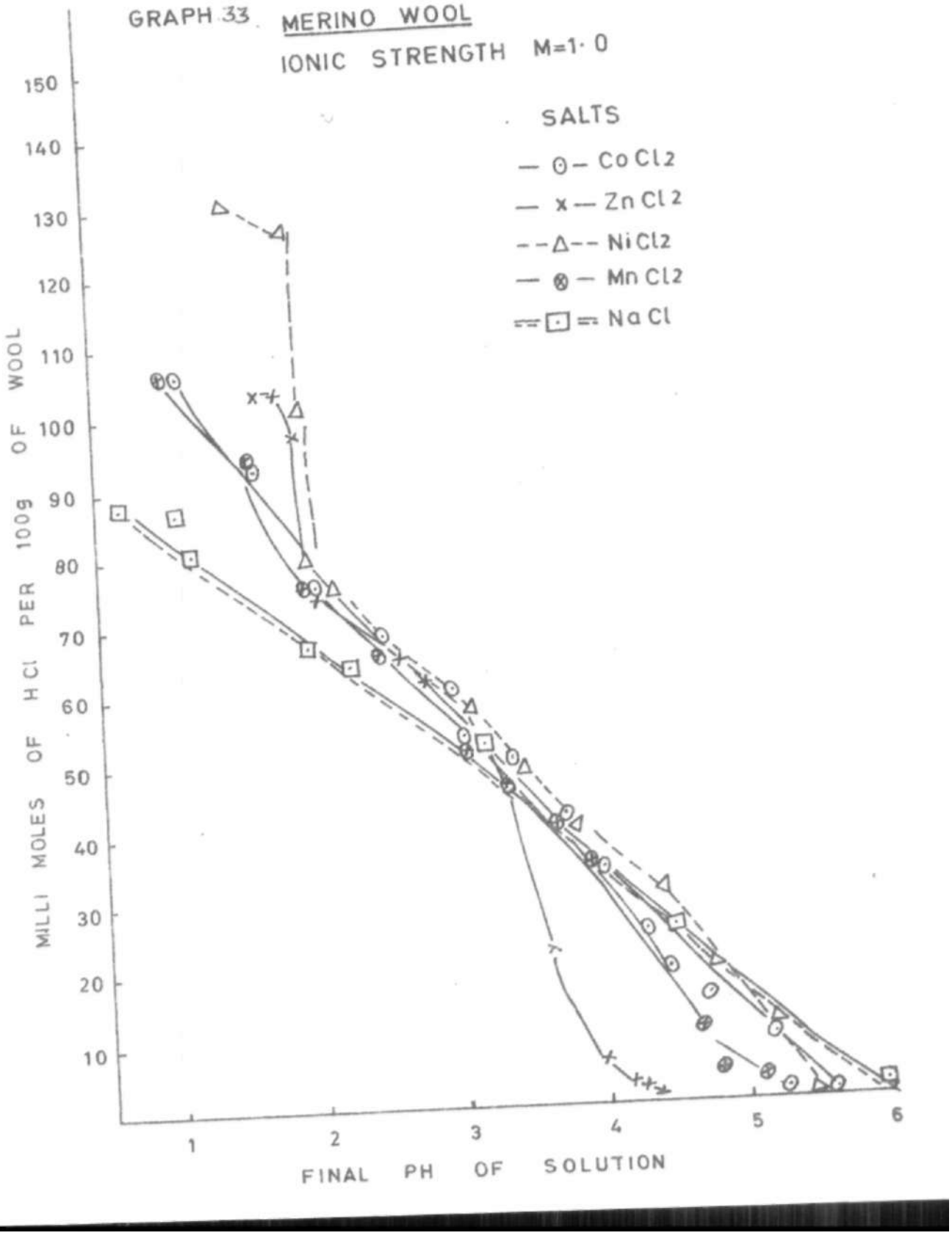
A similar equation can be derived for the metal ion

$$-COO^- + M^{2+} \rightleftharpoons -COO^-M^{2+}$$

(CURVE)

GRAPH 33 MERINO WOOL

IONIC STRENGTH M=1·0



(CURVE)

GRAPH .34

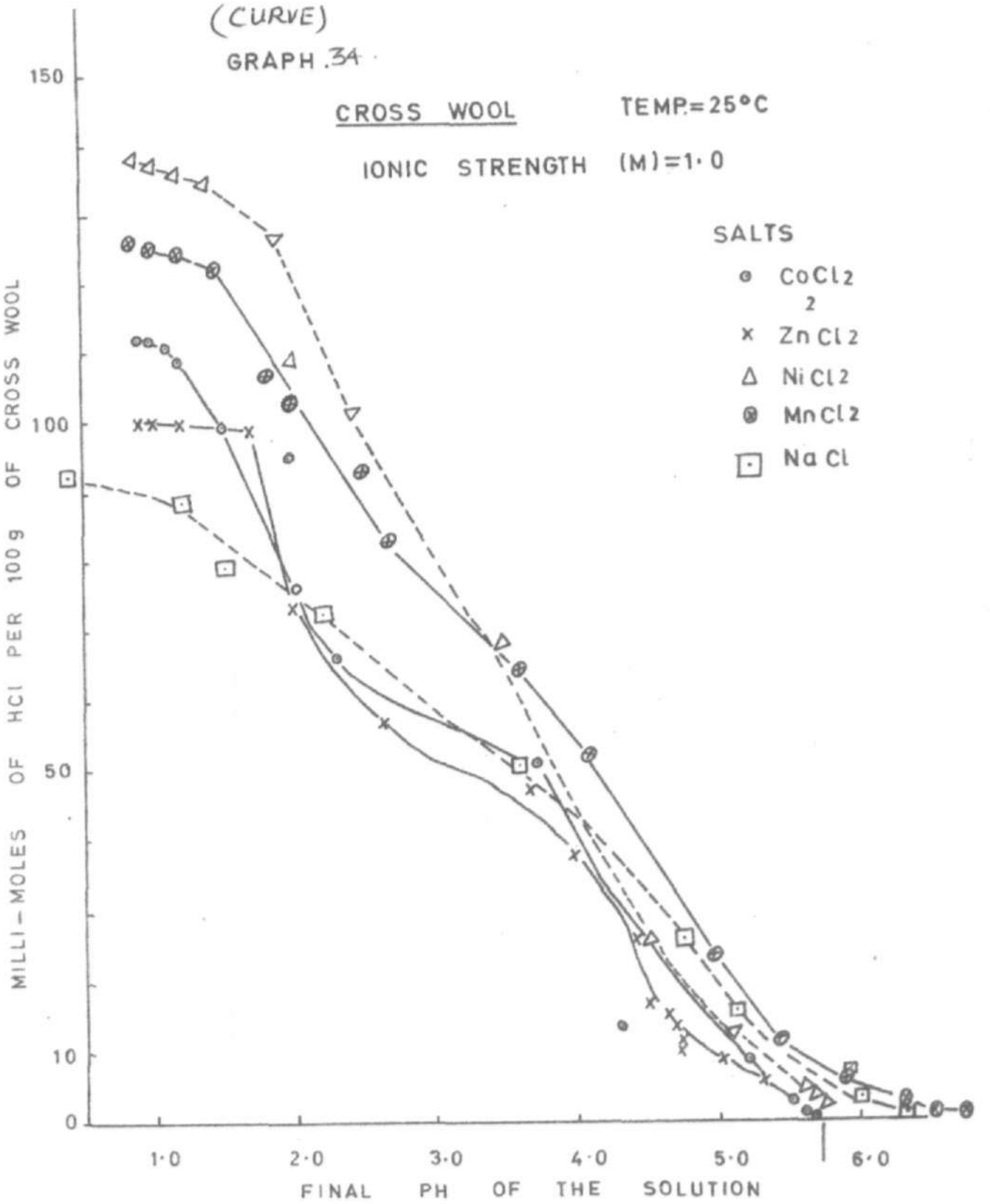
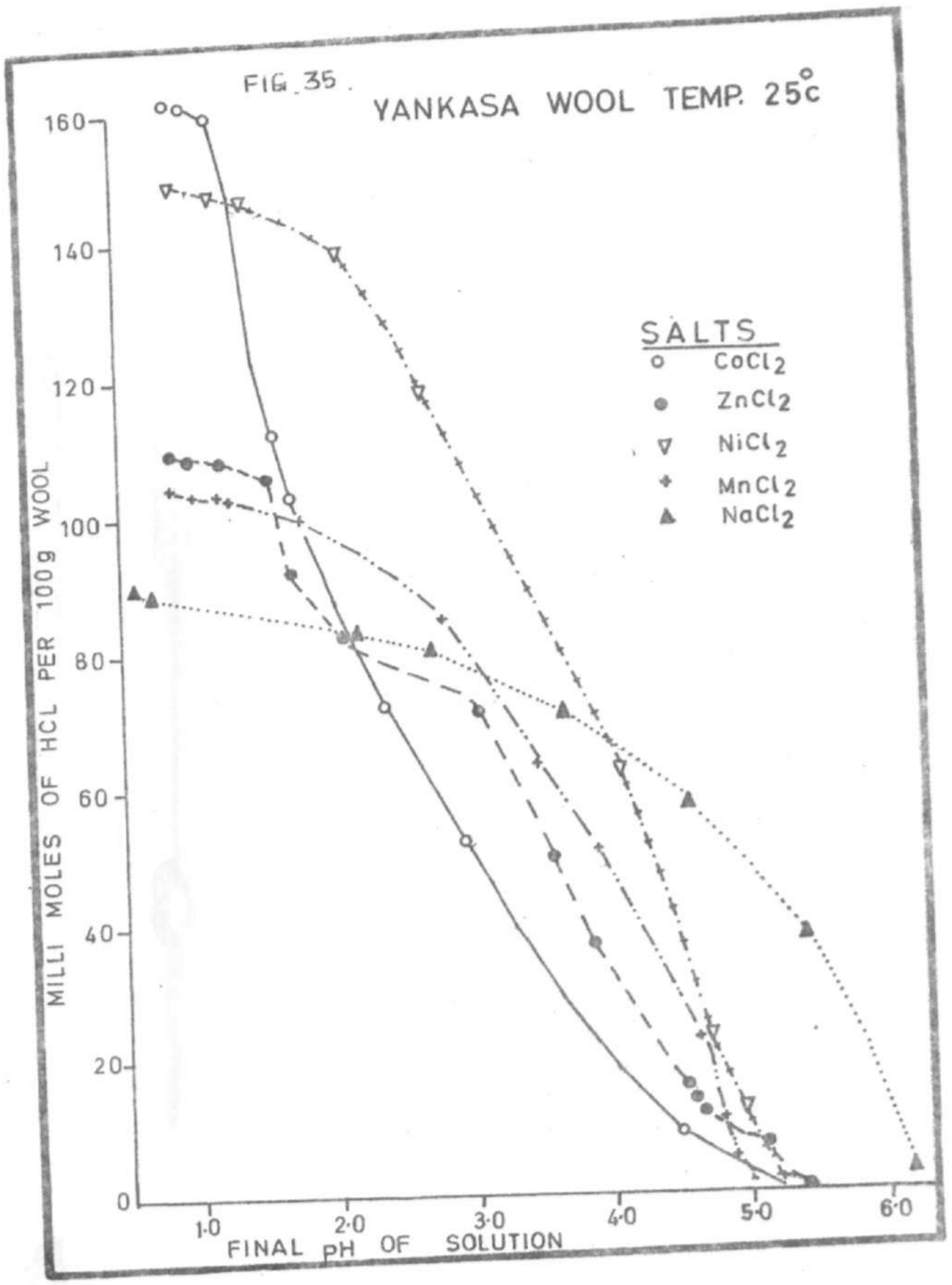


FIG. 35.


YANKASA WOOL TEMP. 25°c
SALTS
CoCl2
ZnCl2
NiCl2
MnCl2
NaCl2
MILLI MOLES OF HCL PER 100g WOOL
160
140
120
100
80
60
40
20
0
1·0
2·0
3·0
4·0
5·0
6·0
FINAL PH OF SOLUTION

Hence metal dissociation constant will be

$$K_M = \frac{[COO^-][M^{2+}]}{[COO^-M^{2+}]} \qquad \text{.....(41)}$$

From equation 38 and 39 and 41 $K_{Ex} = K_m/K$.

5.3.6 Theory of Metal Binding and Interpretation of Titration Curves in Term of pK_o and Metal ion-exchange Constant

The linear Na^+ curve shows log K_{EX} decreasing linearly from $1-\alpha = 0$ to $1-\alpha = 1.0$ which means Na^+ binding is stronger to the non-salt linked groups as to be expected.

For the M^{2+} ions there is more complex behavior. For Merino wool with Mn^{2+}, and Ni^{2+} log K_{EX} first decreases, and increases later. With Co^{2+} there is a smooth but non linear decrease, while with Zn^{2+} there is an increase (up to about $1-\alpha = 0.45$), a decrease (up to about $1-\alpha = 0.6$) and then a final increase.

For Cross wool, all show S-shaped decreasing curves. For Co^{2+} and Zn^{2+} the log K_{EX} is becoming gradually constant. Na^+ curves for Cross is similar to Merino and decreases linearly from $1-\alpha = 0$ to $1-\alpha = 1.0$.

For Yankasa wool with Na^+, Ni^{2+}, Zn^{2+}, Mn^{2+} log K_{EX} is fairly constant to $1-\alpha = 0.5$. while only non-salt linked groups titrate, thereafter having a linear decrease. In case of Co^{2+} a decrease is followed by an increase.

This complex behavior will be the result of one or all of the following factors operating,

(a) different strength of binding to the non-salt linked and salt linked groups; this is illustrated by the linear falls in log K_{EX} for Na^+ with Merino and Cross, the consistency of log K_{EX} for Yankasa wool up to $1-\alpha = 0.5$ where only non-salt linked groups titrate.

(b) the existence of more than one binding equilibrium, giving S-shaped curves, or discontinuties depending how close the binding constants are.

This is exhibited for Merino and Cross wool with the divalent cations.

(c) release of proton from -COOH already protonated at neutrality, by the metal ion exchange, thus increasing the number of $-COO^-$ groups to be in presence of M^{2+} above 90 m. moles/100g.

This is seen clearly in the titration curves, and renders the true values of $(1-\alpha)$ somewhat uncertain and not really comparable between one solution and another.

Discussion on the pK'_o values Merino Wool

(1) $pK_p \simeq 4.4$ for Ni^{2+}, Co^{2+}, Mn^{2+} as compared to the pK_p for Na^+ which is 4.8.

(2) For Zn^{2+}, pK_o is constant at 3.38

(3) For Ni^{2+} and Co^{2+}, pK_o remains fairly constant at 4.4 to about $1-\alpha = 0.2$, then behaving more like the Na^+, pK_q is also operative though somewhat higher than Na^+.

(4) For Mn^{2+}, pK_o falls very rapidly at first.

(5) Lowering of pK_p means dissociation of H^+ is encouraged by the M^{2+} which is expected.

(6) Raising of pK_q means perhaps that the salt-linked has been weakened and large metal cations may be forcing the structure apart somewhat.

(7) Graph of pK'_o verses $1-\alpha$ may be compounded with that of log K_{EX} (metal H^+ exchange constant) vrs $1-\alpha$. They show similar features.

(8) Behavior of Mn^{2+} is somewhat peculiar (but parallel to that for log K_{Ex}) and rises after the rapid fall.

(9) It looks as though pK_q is not very different for all the metallic ions and lies between 3.35 (Zn^{2+}) and about 3.5.

(10) It looks as though for Zn^{2+}, only pK_q is operating. It may be coincidental that pK_p has lowered to pK_q.

5.3.7 Characteristics of the Titration Curves for Merino

In order to start the titration in presence of sodium chloride, the acid is absorbed even at the iso-ionic point; but to start the titration in presence of M^{2+} salt the pH must fall to a value of

5.5 and for Zn^{2+} even less (4.8) before the H^+ is bound. This means that M^{2+} ions are occupying the H^+ binding sites.

It is found that Zn^{2+} ions helps in the titration of HCl. For Co^{2+}, Ni^{2+}, Mn^{2+}, the pH of beginning titration is approximately independent of the ionic strength. It means that the metallic (M^{2+}) binding is more or less complete on the H^+ binding sites already at $\mu = 0.10$, but for the Zn^{2+} this is not so.

At $\mu = 0.1$, the inflexions occur at 52 and ~105 m.moles/100g of wool. This suggest perhaps that two binding sites are present in equal amount (binding of both H^+ and M^{2+}), or a two stage release of M^{2+} from the single type of binding site, e.g.,

$$-COO^{\ominus}....M^{2+}....-OOC^{\ominus} \rightarrow -COOH\ M^{2+}.....^{-}OOC^{\ominus}$$

For $\mu = 1.0$, the inflexions are not so clear. Co^{2+}, Ni^{2+}, and Zn^{2+} have one at 77m. moles/100g, and another at around 110, but Mn^{2+} has at 40m. moles and Zn^{2+} has a third at 10.

There occurs increased hydrogen ion binding in presence of M^{2+} compared with Na^+; it goes up to 130 (Ni^{2+}).

Characteristics of the Titration Curves for Cross Wool

The acid uptake starts at around 5.8 - 5.9. The pH of the beginning of titration in presence of Na^+ is higher than in presence of M^{2+} (5.9 for M^{2+} and 6.6 for Na^+) ; and for M^{2+} it is 6.5. The binding of H^+ is started at 6.6 for $\mu = 1.0$ and at 6.3 for ionic strength (μ) = 0.1.

The titration curves are similar in presence of Zn^{2+} and Co^{2+} in one case and Mn^{2+} and Ni^{2+} in another case. The inflexion only occurs in presence of Co^{2+} and Zn^{2+}. There is no inflexion observed at ionic strength 0.1. This means there is simple titration of -COOH as in presence of Na^{+}. The titration curve of cross wool in presence of Na^{+} is uniform and there is no kink. As in case of Merino there is not much difference either in case of max. acid uptake (90 m. moles/100g) or inflexion at different ionic strengths.

Increased acid binding in presence of M^{2+} is hown as compared to that of Na^{+}; but it is always less than Merino. The acid uptake is in following order: (μ = 1.0) $Ni^{2+} > Mn^{2+} > Co^{2+} > Zn^{2+} > Na^{+}$
138 >125 >112 >102 >90 m.moles/100g.

There occurs one inflexion at 50 for Zn^{2+} and 60 for Co^{2+} but there is no inflexion for Na^{+}, Ni^{2+}, and Mn^{2+} at μ = 1.0.

There are two curves; one is maximum at 50 ≃ 60 and the other from 100 ≃ 130. There are similar curves of Merino also.

Characteristics of the Titration Curves for Yankasa Wool

The pH of the beginning titration is approximately same in presence of Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}. Acid uptake even starts at pH 6.8 in presence of Na^{+}, while in presence of M^{2+}, the pH is ≃5.3 at μ = 1.0.

The pH of the beginning titration also varies with ionic strength (at μ = 1.0 it is 6.8 and at μ = 0.1 it is 7.0).

There is no inflexion up to pH 1.0. The curves are uniform and similar to curves for cross wool. There is not much increase in the acid uptake below pH 1.0.

The maximum acid uptake of Yankasa wool is in the following order: $Co^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Na^{+}$

160 > 150 > 108 > 108 > 104 > 90 m.moles/100g of wool.

Only one curve seems to exist even in presence of M^{2+}.

5.3.8 Comparison of Titration Curves of three Wools:

In presence of Na^{+} the maximum combining capacity for all the three wools is 90 m.moles/100g. ~~Similar shape of the curves is shown for Cross and Merino.~~ Due to same number of $-COO^{-}$ groups are titrating by the Merino and Cross, there is close resemblance among these two wools. Yankasa's behavior is different. The acid uptake is higher in presence of M^{2+} but it is low in presence of Na^{+}. This may be due the presence of high percentage of basic amino groups (arginine, lysine, histidine and terminal amino group (vide chapter: Amino acid analysis).

FIG. 36 MERINO WOOL

Log K VS $(1-\alpha)$ at 25°C

EX

IONIC STRENGTH (M) = 0·1

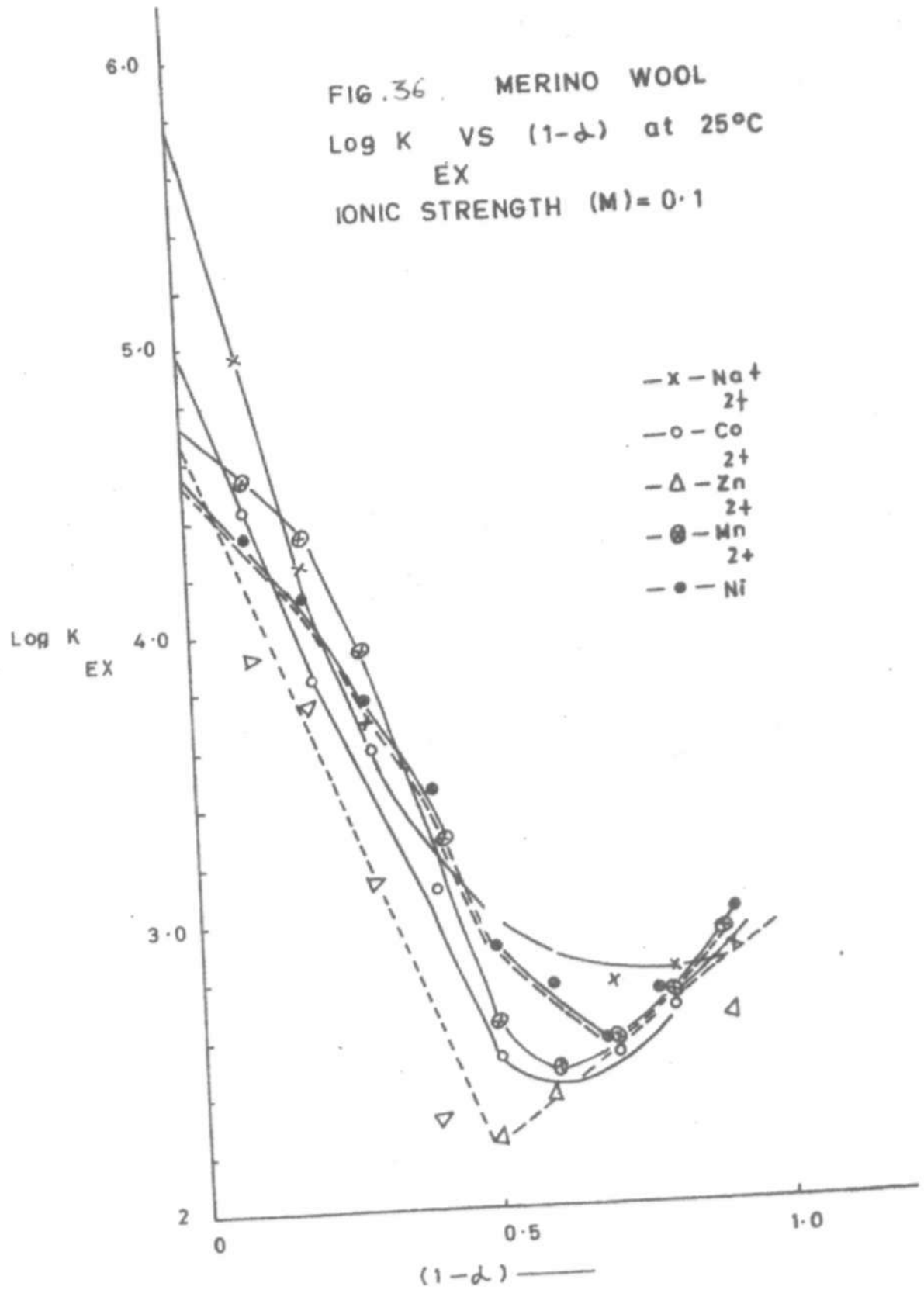


TABLE NO.5.3. MERINO WOOL $pH + \log \frac{1-\alpha}{\alpha} + 0.477 = \log K$

VALUES OF LOG K FOR THE TITRATION OF MERINO WOOL, TEMPERATURE 25°C

$1-\alpha$	NaCl, $\mu = 0.1$		$CoCl_2$, $\mu = 0.1$		$ZnCl_2$ $\mu = 0.1$		$NiCl_2$ $\mu = 0.1$		$MnCl_2$, $\mu = 0.1$	
	pH	Log K	pH	Log K	pH	Log K	PH	Log K	pH	Log K
0.1	5.42	4.96	4.80	4.43	4.4	3.93	4.83	4.36	5.00	4.53
0.2	4.36	4.24	3.95	3.83	3.88	3.76	4.26	4.14	4.44	4.32
0.3	3.58	3.69	3.48	3.59	3.00	3.11	3.66	3.77	3.80	3.91
0.4	3.00	3.30	2.80	3.10	2.06	2.32	3.14	3.44	2.98	3.28
0.5	2.52	3.00	2.04	2.52	1.78	2.26	2.41	2.89	2.14	2.62
0.6	2.22	2.88	1.79	2.45	1.74	2.40	2.12	2.78	1.80	2.46
0.7	1.94	2.79	1.66	2.51	1.68	2.53	1.70	2.55	1.68	2.53
0.8	1.74	2.82	1.59	2.67	1.60	2.68	1.64	2.72	1.62	2.70
0.9	1.46	2.89	1.52	2.95	1.21	2.64	1.57	3.00	1.52	2.95

FIG. 37

MERINO WOOL

Log K VS $(1-\alpha)$ at 25°C
Ex

IONIC STRENGTH (M.) = 1·0°

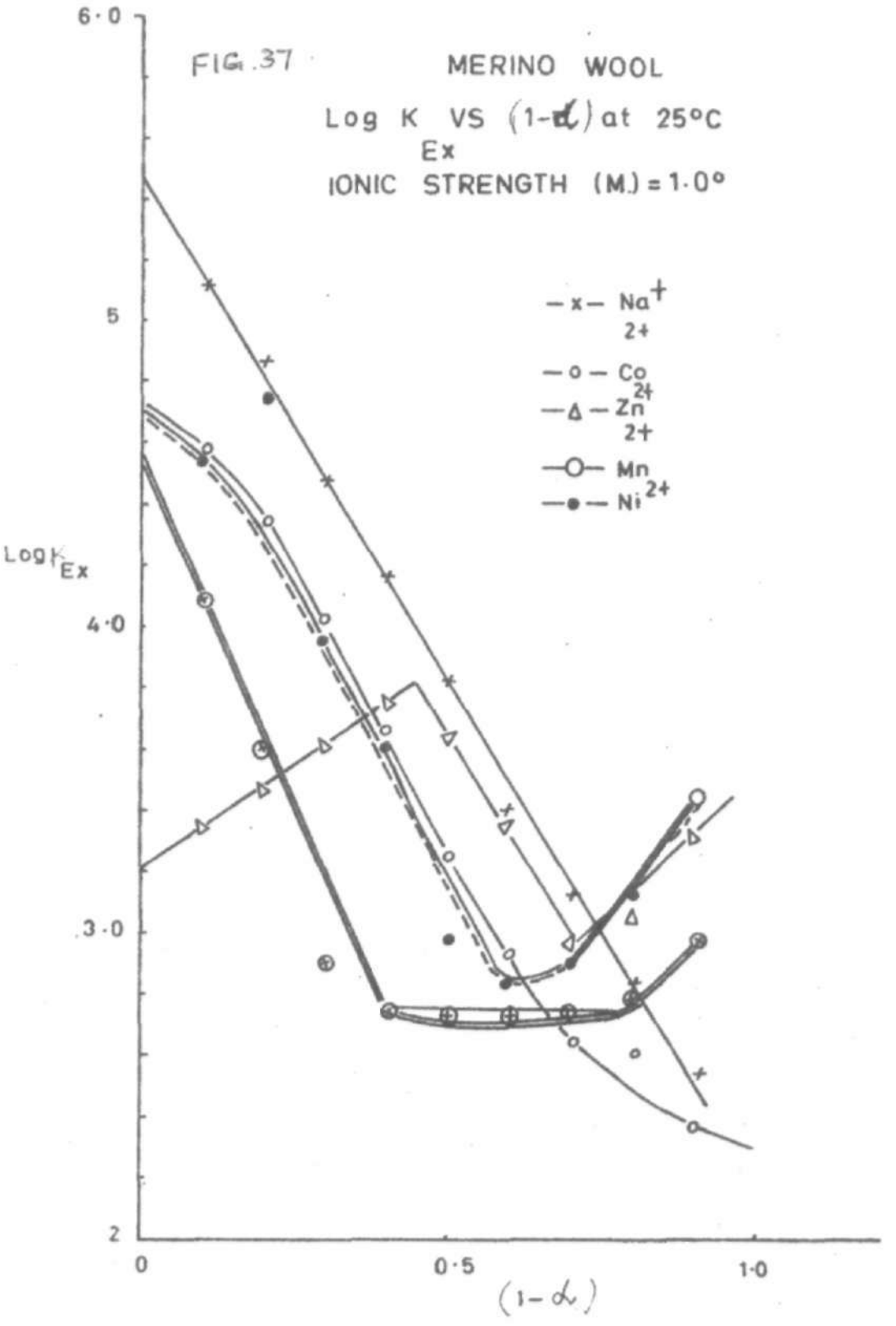


TABLE NO. 5.31 MERINO WOOL.

VALUES OF LOG K FOR THE TITRATION OF MERINO WOOL AT TEMPERATURE 25°C

1 - α NaCl, Γ = 1.0 $CoCl_2$, Γ = 1.0 $ZnCl_2$, Γ = 1.0 $NiCl_2$, Γ = 1.0 $MnCl_2$, Γ = 1.0

	pH	Log K	pH	Log K	pH	Log K	PH	Log K	pH	Log K
0.1	5.58	5.11	5.06	4.59	3.82	3.35	5.00	4.53	4.54	4.07
0.2	4.96	4.86	4.48	4.36	3.60	3.48	4.86	4.74	3.70	3.59
0.3	4.36	4.47	3.92	4.03	3.50	3.61	3.84	3.95	2.76	2.87
0.4	3.85	4.15	3.36	3.66	3.46	3.76	3.28	3.85	2.44	2.74
0.5	3.32	3.80	2.78	3.26	2.16	3.64	2.50	2.98	2.24	2.72
0.6	2.80	3.40	2.25	2.91	2.70	3.36	2.18	2.84	2.06	2.72
0.7	2.28	3.13	1.83	2.63	2.14	2.99	2.06	2.91	1.90	2.75
0.8	1.74	2.82	1.53	2.61	2.98	3.06	2.05	3.13	1.72	2.80
0.9	1.22	2.55	0.93	2.36	1.91	3.34	2.02	3.45	1.56	2.99

FIG.38

CROSS WOOL

Log K VS $(1-\alpha)$ at 25°C

IONIC STRENGTH (M)=1·0

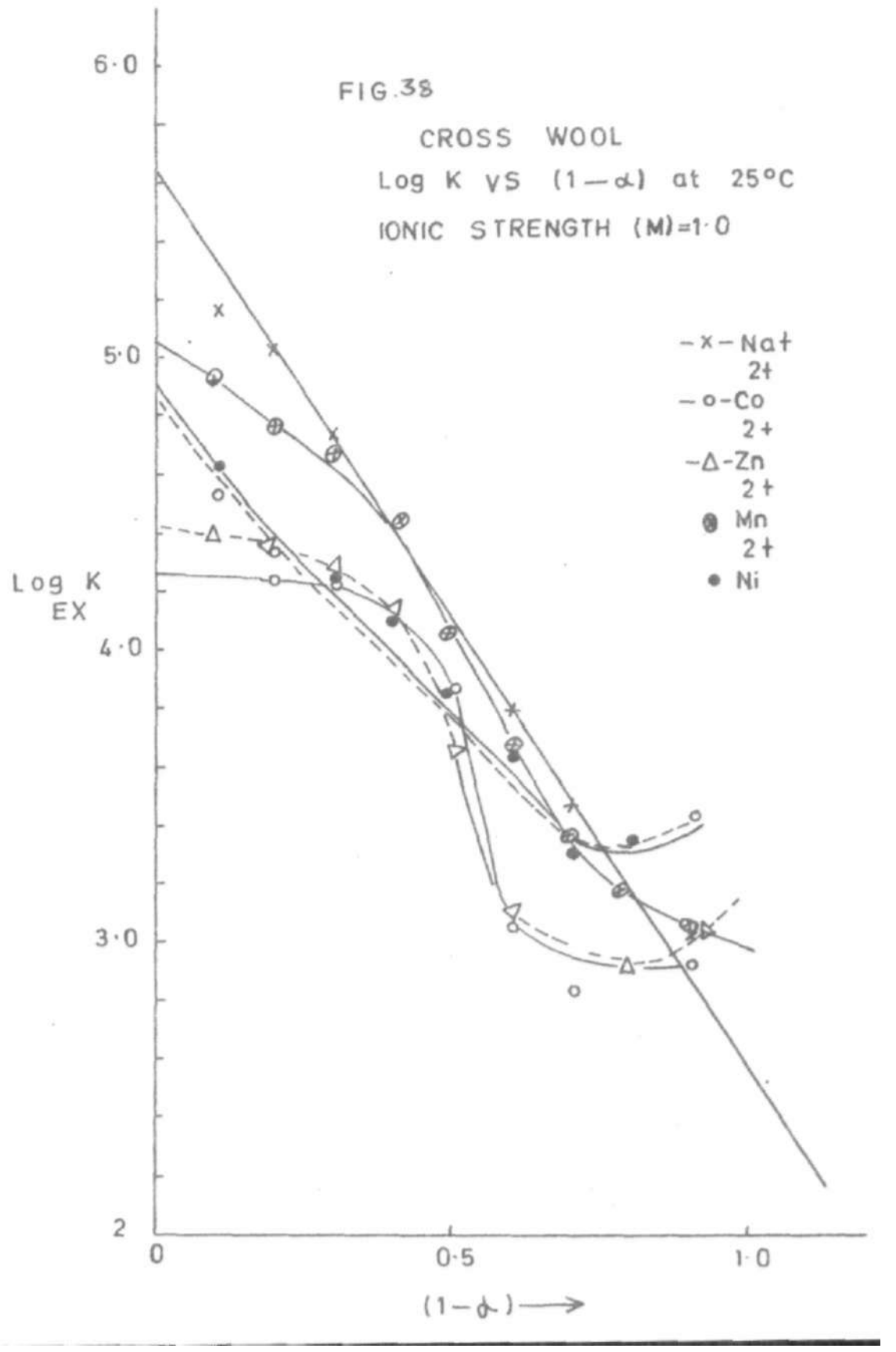


TABLE NO. 5. 32 — CROSS WOOL

VALUES OF LOG K FOR THE TITRATION OF CROSS WOOL. TEMPERATURE 25°C

1 - α	NaCl, μ = 1.0		$CoCl_2$, μ=1.0		$ZnCl_2$, μ=1.0		$NiCl_2$, μ=1.0		$MnCl_2$, μ=1.0	
	pH	Log K	pH	Log K	pH	Log K	pH	Log K	pH	Log K
0.1	5.64	5.17	5.00	4.53	4.86	4.41	5.10	4.63	5.40	4.93
0.2	5.14	5.02	4.36	4.24	4.49	4.37	4.46	4.34	4.90	4.78
0.3	4.62	4.73	4.10	4.21	4.16	4.27	4.10	4.21	4.56	4.67
0.4	4.12	4.42	3.82	4.12	3.84	4.14	3.80	4.10	4.14	4.44
0.5	3.60	4.08	3.38	3.86	3.16	3.64	3.38	3.86	3.61	4.09
0.6	3.12	3.78	2.40	3.06	2.44	3.10	2.96	3.62	3.00	3.65
0.7	2.62	3.47	1.96	2.81	2.13	2.98	2.45	3.30	2.53	3.38
0.8	2.10	3.18	1.84	2.92	1.99	2.97	2.25	3.33	2.10	3.18
0.9	1.60	3.03	1.48	2.91	1.60	3.03	1.99	3.42	1.64	3.07

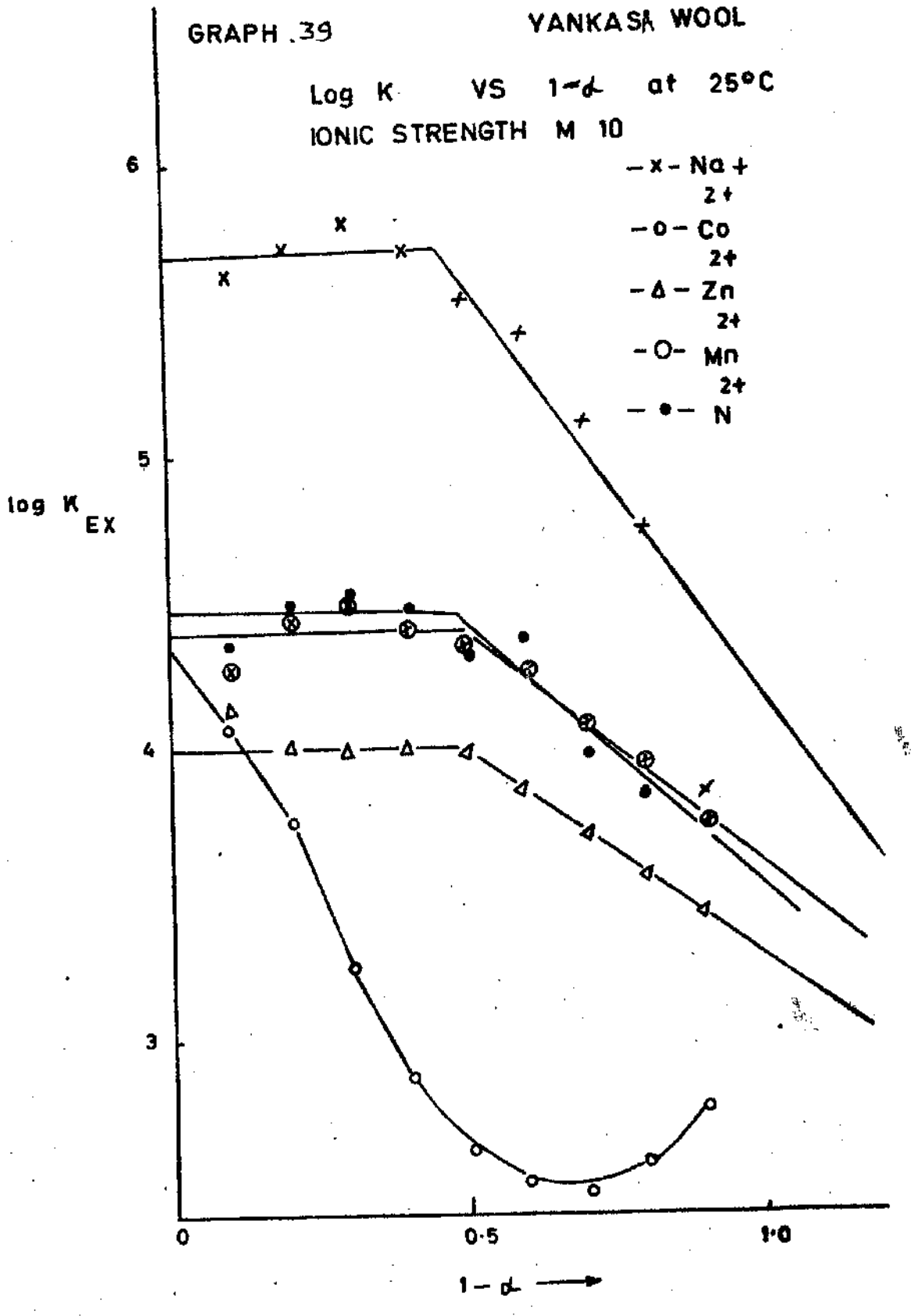

GRAPH .39
YANKASA WOOL
Log K VS 1−α at 25°C
IONIC STRENGTH M 10
−x− Na+
−o− Co2+
−Δ− Zn2+
−O− Mn2+
−•− N
log K EX
6
5
4
3
0
0·5
1·0
1 − α

TABLE NO. 5.33 YANKASA WOOOL

VALUES OF LOG K FOR THE TITRATION OF YANKASA WOOL AT TEMPERATURE 25°C

1 - ϰ	$NaCl$, $\mu = 1.0$		$CoCl_2$, $\mu = 1.0$		$ZnCl_2$, $\mu = 1.0$		$NiCl_2$, $\mu = 1.0$		$MnCl_2$, $\mu = 1.0$	
	pH	Log K	pH	Log K	pH	Log K	pH	Log K	pH	Log K
0.1	6.06	5.59	4.54	4.07	4.64	4.17	4.82	4.35	4.74	4.27
0.2	5.90	5.78	3.87	3.75	4.12	4.00	4.60	4.48	4.56	4.44
0.3	5.70	5.81	3.14	3.25	3.90	4.01	4.40	4.51	4.38	4.49
0.4	5.48	5.78	2.58	2.88	3.72	4.02	4.16	4.46	4.10	4.40
0.5	5.20	5.68	2.14	2.62	3.48	3.96	3.85	4.33	3.85	4.33
0.6	4.74	5.40	1.86	2.52	3.20	3.86	3.72	4.38	3.58	4.24
0.7	4.24	5.09	1.64	2.49	2.90	3.75	3.13	3.98	3.24	4.09
0.8	3.60	4.68	1.50	2.58	2.49	3.57	2.74	3.82	2.86	3.94
0.9	2.42	3.85	1.34	2.77	2.00	3.43	2.26	3.69	2.29	3.72

5.3.9 Interpretation of Metal Binding in the Light of Amino Acid Composition

Table .No.534.

Amino Acid (Acidic) m.moles/100g of Wool

Amino Acid	Merino	Cross	Yankasa
ASP.	56.6	55.5	54.5
GLU.	94.4	87.0	118.0
Total	151.0	142.	172.5

Table No. 5.35

Amino Acid (Basic) m. moles/100g of Wool.

Amino Acid	Merino	Cross	Yankasa
LYS.	25.3	24.0	29.1
HIS	6.1	5.9	5.9
Total	31.4	29.9	35.0

Table No. 5.36

Amino Acid (All Basic) m.moles/100g of Wool.

Amino Acid	Merino	Cross	Yankasa
ARG.	62.5	57.0	59.7
LYS.	25.3	24.0	29.1
HIS.	6.1	5.9	5.9
Total	93.9	86.9	94.7

With M^{2+}

Before titration begins, the -COOH group at neutrality has become $-COO^{-}M^{2+}$ and can be titrated. Subsequently this is why the acid combining capacity is often greater for $\mu = 1.0$ than for $\mu = 0.1$ in presence of M^{2+} and we find the acid uptake goes 150 m. moles/100g. $-COOH + M^{2+} = -COOH^{-}M^{2+}$. The experimental values are given in the Table 5.28. On the basis of amino acid composition the calculated values for different wool is:

Merino	151	m.moles/100g of wool.
Cross	142.5	" " " "
Yankasa	172.5	" " " "

From the calculated data of the acid amino acid groups one must expect that there should be more acid uptake in case of Yankasa wool which is shown as compared to other varieties of wools. Besides this, the presence of metallic ions as well as the increased concentration will facilitate the titration of wools.

When we go through the concentration of various basic amino groups in the given wool we find the following order:

Total Basic Amino Groups

m.moles/100g of Wools.		Acid Uptake by the Wools (Observed from titration data)
Merino	94.9	89.32
Cross	86.9	88.2
Yankasa	94.7	90.2

Reasonable agreement is found between the calculated values of these groups from the titration data and the amino acid composition.

As previously stated, same number of titratable carboxyl groups (86 ± 94) are present due to the ionization of lysine, histidine and arginine groups. Reasonable agreement is found between the calculated values of these groups from the titration data and the amino acid composition.

In general, an inflexion occurs at about m.moles/100g = 50 for Merino and Cross, but there is no inflexion for Yankasa in presence of M^{2+}. Two possibilities might exist. Firstly, M^{2+} has perhaps bound only to the non-salt linked groups; secondly, the formation of $-COO^{-}M^{2+}$ as well as $(-COO^{-})_2M^{2+}$ both simultaneously fuctioning ; or thirdly, some other explanation is required to fit the experimental data to the number of amino acid groups.

Zinc has its own chacteristic, it has shown a first inflexion at about m.moles/100g = 10 at the ionic strength μ = 1.0 for Merino and Cross.

For Yankasa, the inflexion at 50 m.moles does not exist which was expected. The abnormal behavior of Yankasa wool may be due to lesser number of salt-linked groups as compared to the Merino and Cross. Yankasa has shown a inflexion at about 75 m.moles and also in presence of Co^{2+}. Question arises: is the structure of Yankasa wool so different that it renders both the possibilities to to be ruled out, i.e. $(-COOM^{2-}$ and $(-COO)_2M^{2-}$; or due to structural difference some other factors are operating? Or is the inflexion at 75 m.moles evidence that only $\frac{1}{4}$ of the groups are salt-linked?.

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Chapter 6

INFRA-RED SPECTROSCOPY

6.0 Infrared Spectroscopy

6.1 Introduction:

Infra-red spectroscopy is a very useful and handy tool to illustrate the different functional bonds present in the keratin. The most common bonds are ionic bonds, covalent bonds and hydrogen bonds. Atoms are always in constant motion, and when they are joined by the bonds into the molecules, their motions resemble those of a system of weights connected by springs out of many vibrations, two of which are basically different types of motion. In addition to the principal modes, hybrid vibrations also occur when coupling takes place between several of these. So far the most fruitful application of polypeptide chain in the study of the orientation and configuration of the polypeptide chain in solid specimens, are more helpful.

On the basis of the two phase system (α-keratin and β-keratin) as suggested by the X-ray and electron-microscopic evidence one may expect two different structures to be obtained from wool. The one an α-helical protein of high molecular weight and a non-helical protein. All the available evidences lead to the fact that in the

solid state, poly-peptides and proteins have a strong tendency to adopt either an α-helical or an extended configuration characterized respectively by regular spatial arrays of intra- and inter-molecular hydrogen bonds. Due to extreme sensitivity of amide vibrations to the molecular environment it has been found that two types of configurations have provided different absorption frequencies.

Elliott and his co-workers (1,2) had established correlations between the amide frequencies of synthetic poly-peptide in helical α and extended β configurations. Their findings are also applicable to the fibrous protein at least in part. α and β-keratin exhibit the characteristics generally observed in protein spectra, are amide A, I, and II bands The frequencies of the prominent absorption bands, together with their dichroism, designation, and assignment are given in the Table 6.1. The Table includes the fundamental bands due to non-crystalline phases, as well as bands in the overtone region of the spectrum.

The origin of most of these bands has been studied for many years and has provided useful information regarding the keratin structure. Ambrose and Elliott (3) from the parallel dichroism of the amide A and I bands, concluded that the N-R and C=O groups in keratin were preferentially oriented parallel to the fibre axis. They also established certain frequency créteria of the amide I and II bands for both α and β structure.

The amide A and B bands which arise from the N-H stretching vibration in proteins are found in the 3μ region at 3290cm^{-1} and 3060cm^{-1} whilst various C-H bands are detected in the range of 3,000 - 2800cm^{-1}. In addition to these features, a weak band appears near 1230cm^{-1} (amide III) which has assigned to the N-H in plane deformation coupled with stretching mode.

6.2 Determination of Configuration:

The original interpretation of the spectrum of extended keratin in terms of a parallel pleated - sheet structure has subsequently been shown unlikely to be correct, as the presence of the (weak) perpendicular component of the amide I band near 1700cm^{-1} indicates that a least, part of the crystalline material is in the antiparallel arrangement. The nature of the principal infra-red absorption bands, indicative of the characteristic bending and stretching frequencies of the N-H band and the stretching frequency of C=O band, had been used to distingish between the crystallographic forms of keratin (4,5). Miyazawa and Blout concluded that the absence of a weak band at 1690cm^{-1} was the indication of a parallel chain structure of β-keratin. Although Parker (5) found this band in the structure of β-keratin and it has the appropriate dichroism, i.e., the maximum absorption at this frequency, 1690cm^{-1}, occurs with the electric vector of polarized radiation perpendicular to the fibre

axis, it is doubtful whether such interpretation of the infrared spectra of keratin, can be made, in view of the evident heterogeniety of wool fibre.

According to the finding of Miyazawa and Blout (6,7) and Elliott and Bradbury (8) any model for the α-keratin must have both the C-O and N-H bonds, and therefore the hydrogen bonds connecting them, parallel to the fibre axis. β-keratin in contrast must have hydrogen bonds normal to the poly-peptide chain axis. The cross -β form shows the interesting anomoly of having its absorption frequencies close to those of the β-form, but its hydrogen bonds parallel to the fibre axis as in the α-helix.

6.3 Interaction of divalent metal ions with the Wool:

Proteins and poly-peptides possess large numbers of potential sites for interaction with metals resulting complex formation. The complex formation or chelation, is an important phenomenon in protein interaction. Whenever chelation occurs, the combining sites on the protein must satisfy certain steric requirements. The possible number of sites for binding are less than expected. In general, the ligand groups in the native protein are not free to cluster around a metal ion. Thus, while the protein contains many ligands, each metal ion may combine with only one. It is not always the metal ion but water molecules may also complete co-ordination. Metals, in general, combine at the same sites as hydrogen.

It has been shown by several authors (11,12,13) that virtually all of the potential reactive groups have been shown to be involved in the binding of metals. However, in all cases, the uptake of metal was exceedingly small. In interaction of zinc ions with albumin, for instance, the maximum binding for zinc was 8g, atom per 100,000g of protein, and for cadmium ions it was, 4.0g atoms for a similar amount of protein (13).

TABLE 6.1 PROMINENT INFRA-RED ABSORPTION BANDS IN DRY KERATIN

SPECIAL REGION DESIGNATION		α	β	RANDOM COIL ASSIGNMENT
OVERTONE		4970 (II)		amide A + amide I
		4870 (I)		amide A + amide II
		4590 (0)		amide A + amide III
		4360		CH_2 combination modes
		4240 (II)		CH_2 combination modes
Fundamental	Amide A	3286 (II)	3268 (I) 3310	Fermi resonance of NH stretching and 2X amide II
	Amide B	3065 (II)	3075 (I)	" " " " " "
		2960		CH_2 and CH_2 Symmetric and anti-symmetric stretching modes.
		2929		" " " " " " "
		2875		" " " " " " "
		2853		" " " " " " "
	Amide I	1655 (II)	1627 (I) 1650	C=O Stretching 80%
			1697 (II)	" " 80%
	Amide II	1545 (I)	1522 (II) 1520	N-H bending 60% and C-N Stretching 40%
		1450	1450	C-H bending
	Amide III	1250 (I)		N-H bending 30% and C-N stretching 40%

6.4 EXPERIMENTAL

Clean dry samples of Merino and cross were ground to a fine powder in a speed vibration mill for approximately five minutes. Care was observed during the grinding in order to avoid excess heat and thus prevent degradation. 3 mg. of fine powder thus obtained, were mixed with potassium bromide (spectroscopic grade) in the weight ratio of 3:150 and placed subsequently in an evacuable disc. Vacuum was applied and a considerable pressure exerted on the mixture so that a thin and transparent disc was obtained. Liquid solutions spectra were obtained using two rock salt plates. In between, a drop of solution was placed and cell thickness adjusted to obtain satisfactory maximum absorption peaks. The spectra were recorded with Perkin Elmer Model 21 and Unicam SP.1200 spectrophometer. The spectrometer was frequently calibrated using a polystyrene film. The absorption was obtained between 4000 - 1200cm^{-1} and measurements were found to be reproducible to $\pm 1.cm^{-1}$.

Similar method was repeated with treated wools. The conditioned wool (1.00g $\pm$ 0.001) was immersed in 100cm^{-3} $ZnCl_2$ (0.33), $MnCl_2$ (0.33) $NiCl_2$ (0.33) and $CoCl_2$ (0.33) in four different polythene bottles. 1.0cm^{-3} of 0.1M HCl was added to each bottle. The bottles were kept 72 hours (vide page 147) for equilibrium.

After 72 hours treatment, the wool was taken out and washed with distilled water. Water collected from the wool washing was transferred to a volumetric flask and made to one litre. The quantity of metal ions was estimated using Atomic Absorption spectrophotometer Model A3000. The method is based on flame photometry (10).

The washed and treated fibre was thoroughly dried and powdered to obtain the spectra with the help of spectrophotometer.

6.5 RESULTS

The absorption spectra of Merino Cross and Yankasa are given on page 200

Table 6.2 MERINO WOOL

% Absorption of intensity (vide Fig. 40)

Pure Merino		Zn^{2+} treated		Mn^{2+} treated		Ni^{2+} treated		Co^{2+} treated	
Frequency	Absorption	Frequency	Absorption	Frequency	Absorption	Frequency	Absorption	Frequency	Absorption
Cm^{-1}	%	Cm^{-1}	%	Cm^{-1}	%	Cm^{-1}	%	Cm^{-1}	%
3361	71.06	3361	73.82	3367	96.0	3361	80.37	3361	77.57
2899	53.26	2909	59.81	2920	82.24	2908	76.63	2908	71.96
1613	71.03	1600	78.50	1613	100.00	1594	97.18	1600	87.84
1471	67.28	1471	74.74	1481	95.32	1471	92.49	1484	84.10
1198	57.94	1198	67.2	1198	87.84	1198	83.18	1205	77.63
1020	52.34	1031	59.81	1031	81.30	1031	71.96	1031	69.15

Table 6.3

CROSS WOOL

% Absorption

Pure		Zn^{2+}		Mn^{2+}		Ni^{2+}		Co^{2+}	
Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %
1600	88.2	1600	84.8	1600	96.2	1600	88.8	1600	94.2
1480	92.2	1480	78.6	1480	88.8	1480	12.8	1480	98.2
1210	63.0	1210	60.0	1210	66.6	1210	53.0	1210	67.2
1163	49.8	1163	52.2	1163	53.4	1163	49.2	1163	51.0

Table 6.4

YANKASA WOOL

% Absorption

Pure		Zn^{2+}		Mn^{2+}		Ni^{2+}		Co^{2+}	
Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %	Frequency Cm^{-1}	Absorption %
3300	65	3020	70	3300	68	3300	78	3100	60
2990	52	2920	89	2920	91	3000	52	2920	91
2940	59	1640	79	1660	77	2960	61	1660	74
2900	60	1580	72	1600	60	1680	83	1590	61
1660	83	1530	77	1540	73	1600	70	1535	71
1580	67	1480	72	1500	62	1480	59	1500	63
1520	77	1460	82	1485	88	1460	60	1475	88
1480	64	1420	69	1420	57	1410	61	1420	63
1420	62	1380	79	1380	77	1380	55	1380	84
1390	65	1240	68	1240	52	1240	59	1240	61
1280	60								

MERINO

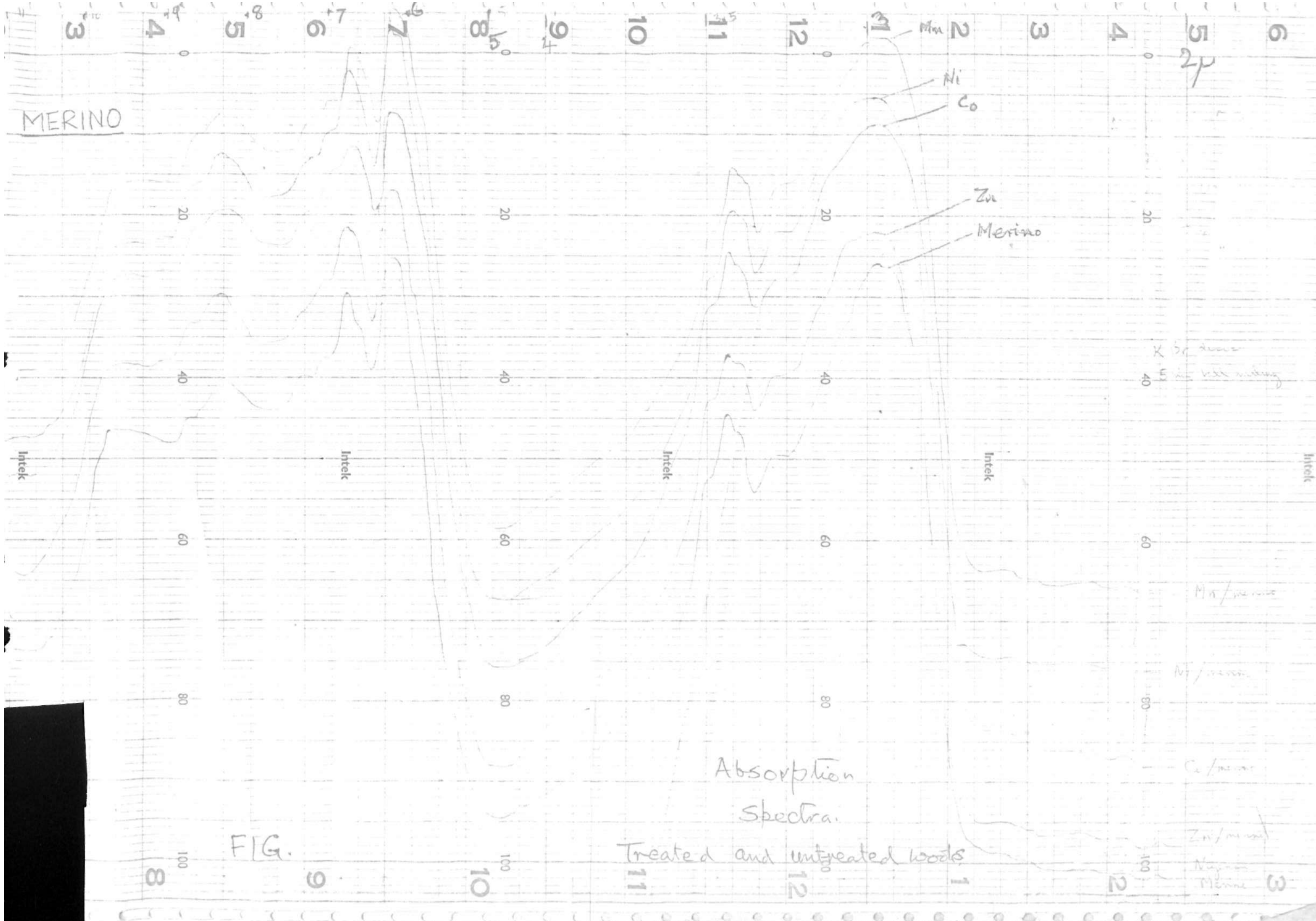
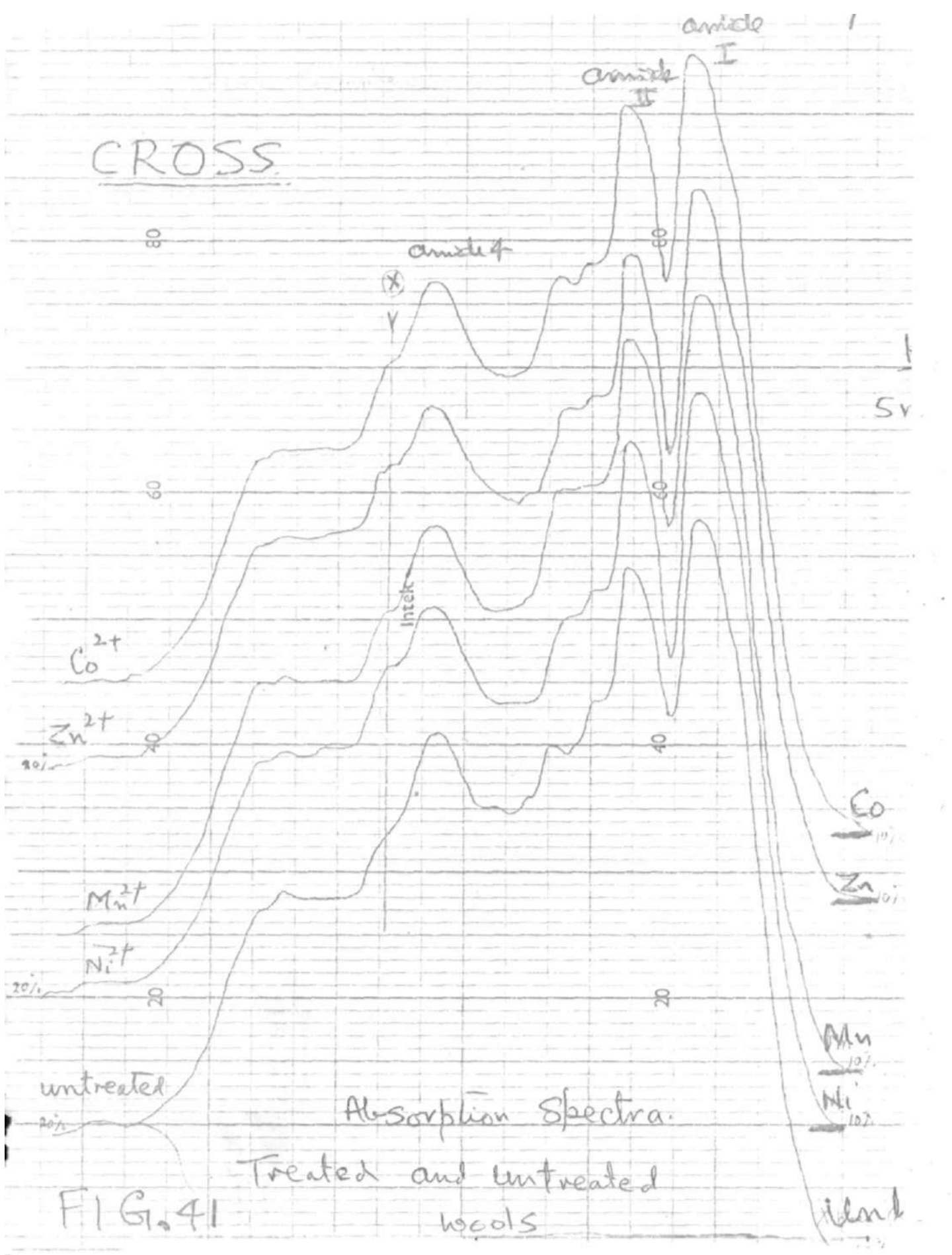


FIG.

Absorption Spectra.

Treated and untreated wools



Absorption Spectra.
Treated and untreated wools

FIG. 41

(3) There is no sign of metal carbonyl bond.

(4) The vibration frequencies of N-H stretching for α-structure 1530 - 1550cm^{-1} and 1520 - 1535cm^{-1} of β-structures are mostly out of phase (shifted).

Two things are apparent from the spectra:

(1) The fibres have been degraded to the same extent since the amide II bands of the treated sample have increased to approximately the same extent. This may be due to hydrolysis (72 hours) between pH (2-4).

(2) Complexing of metal ion has influenced amide I bands; and a 1163 (for Cross) on amide 4 band.

In case of Cross and Merino wools the order of effect on amide I seems to be $Ni^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+}$ ~~which has got close~~ while resemblance in the order of absorption of metal ions by Merino is sounder.

Merino $Ni^{2+} > Zn^{2+} > Mn^{2+} > Co^{+}$

2.01 > 1.52 > 0.74 > 0.127 g. atom/100g of wool.

More-over, the non-uniform behaviour of three wools have been observed in chapter 3, in which the elastic properties (the work to stretch) have been investigated.

In this connection, it is suggested that more exhaustive quantitative work should be carried out to study number of shifting of peaks and to support the idea of complex formation or exchange of metal ions by hydrogen.

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APPENDIX I

GLOSSARY OF WOOL TERMS

Apparel wools. Any wool that is manufactured into cloth for use as clothing.

Astrakan: A grade of Karakul lambskins that is less lustrous, with longer hair and more open curl than on some other grades.

Bale: Wool production for some countries is given in bales rather than as pounds or tons. Australian and New Zealand wools weight about 330 pounds per bale; South American bales weigh approximately 1,000 pounds.

Blood: The term blood is used along with half, three-eights, quarter, and low quarter to indicate degree of fineness of wool. These terms now have no relation to the breeding of the sheep from which the wool was obtained.

Botany: A term applied to some goods made from fine wool and Also applied to fine wool from Australia.

Braid: The coarsest of the United States grades of Wool. Most braid wool is lustrous and is from the longwool breeds.

Breaking Length: It is the length of the specimen which will just break under its own weight when hung vertically.

Breaking Load: This is the load at which the specimen breaks, usually expressed in grams weight or pounds weight.

Breaking Extension: It is the extension of the specimen at the breaking point.

Bucks or buck wool: The wool from rams. It is distinguished from ewe or wether wool by its odour and usually heavier shrinkage caused by a greater amount of grease. It often sells at about one-half or two-thirds the price of other wool, partly because of its shrinkage and also because it may have coarse hairs mixed with the wool fibers.

Burry wool: Wool that contains burrs from any of the plants. Such wool requires special processing in manufacturing, is higher in shrinkage, and hence sells at a discount compared with "clear" (free-of-burrs) wool. Light burry and hard burry are used in referring to the amount of burrs. Fine burry, medium burry refer to the grade of the wool.

Cape Wool or Capes Wool from South Africa.

Caracul: A type of Karakul lambskin.

Card: A many-toothed tool or machine used to open the wool fibres by opening the locks or tufts of wool. Hand cards are now used chiefly in the fitting of show sheep.

Carding: One of the first steps in the preparation of secured wool for further processing. In the process the wool fibres are separated from other fibres in the locks or bunches of wool.

Carpet Wool: Low-grade coarse wool, generally from unimproved sheep, used in the manufacture of carpets and rugs. It may also be used for coarse wearing apparel. Some rugs are made from finer grades of wool than that usually thought of as carpet wool.

Clip: The process of shearing, clipping. The weight or type of the wool from a certain flock. Also, the yearly total production.

Clothing wool: Wool that is too short to be combed. Hence, the basis of designation is one of length. These short-fibred wools are used chiefly in the manufacture of woolens and felts. Sometimes called woolen wools.

Combing: An operation in the manufacture of worsteds that separates the short fibres, known as noils, from the longer fibres which are combed into a continuous strand in which the fibres are parallel. The finished product is known as top.

Combing wool: Wool that is strong and is long enough to be combed. In the United States Standards, fine combing wool is two inches or more in length. The length increases at least one-forth inch for each grade as the wool gets coarser.

Comeback: A sheep or wool from a sheep that has a crossbred dam and a fine-wool sire (Merino). Wool of this kind has good length and is about half blood or 58's and 60' quality.

Fellmonger. A dealer in pelts and pulled wool.

Felting: The interlocking of wool fibres, which may be caused by heat, moisture, and friction.

Filling (weft): Threads that run crosswise in a fabric and thus fill in between the warp.

Fleece wools: A trade term for wool from the eastern and central states of America.

French combing: Wool that is shorter than strictly combing but yet long enough to comb on French combs. It is longer than clothing wool.

Fribs: Short, dirty bits of wool or those tufts that result from second cuts during shearing.

Frowsy: Wool that is dry and lifeless without distinct crimp due to weathering or to poor quality or both.

Fulling: A step in woolen manufacture whereby the cloth is shrunk, the fabric is "faced," and the weave pattern is covered.

Gare: A term meaning straight, coarse, usually lustrous fibres, sometimes incorrectly called kemp, that are mixed with fine fibres. Often found on the folds of fine-wool sheep.

Grade: A means of designating wool according to the fineness of fibre.

Grading: The process of determining the grade of wool. It is done by examining the unopened fleeces and sorting them into lots according to fineness. As this is done the fleeces are also classified on the basis of length of the fibres.

Grease wool: Wool in the condition in which it is shorn, before washing or scouring.

Gummy : Grease wool that has an excessive amount of yolk or scoured wool that still has some yolk in it.

Hank : A measure of length for yarn; a hank of worsted yarn contains 560 yards.

Hoggett (H-ogg) wool: A term used to designate the first fleece from a sheep.

Hookean Stress: It is the stress at the point where Hooke's law can be truely applied.

Kemp: A chalky white, brittle, weak fibre which, found mixed with normal fibres of a fleece, constitutes a very serious defect. Kemp will not take dyes and lacks strength.

Lamb's wool: Short wool that is supposed to be from lambs not over 7 or 8 months of age. Some wool is graded as lambs' wool and is from lambs of 12 to 14 months of age. It is soft and has less felting properties than sheep wool.

Lanolin: Refined yolk or wool grease. It has many uses among which are various cosmetics.

Looks: Pieces of wool loosened from the main fleece and packed separately in the Australian method of packing wool.

Lofty: Wool or a woolen fabric that has "life" or springiness when compressed and is bulky in comparison with its weight. Lofty wool is light in condition and has very even, distinct crimp.

Luster wool: Wool that shines because it reflects more than the usual amount of light. It is chiefly from the long-wool breeds.

Modock: A term formerly used in referring to wool from range lambs that had been fed in the farm states. Now called fed-lamb wool.

Mohair: The fibre from the Angora goat.

Mouton: A modern fur made by the chemical treatment of the wool on sheep skins.

Murrain: Same as dead wool. Detected by graders by its odour.

Mushy: Wool that is dry, weathered, and wasty. Same as frowsy.

Noils: Short fibres removed in the process of combing. They are useable in the woolen industry.

Off-sorts Fleeces or parts of fleeces that are rejected as unsuitable for the regular lots of graded wools because of being badly stained, having undesirable colour, et cetera. Rejects.

Pelts: The skin and wool together.

Persian lamb: A very desirable, tightly curled, highly lustrous Karakul skin.

Picklock: Formerly a grade of very fine wool. Obsolete.

Plasticity: Under a constant large load, instantaneously applied, animal fibres elongate rapidly by about 30% in cold water and then continue to creep for a prolonged period. In the post-yield region, after the initial extension at constant load, $\log (E_{lim} - E) = a + kt$, where t is the time of extension, E is the extension and E_{lim} is the limiting extension (usually 75 - 80% for Lincoln wool) a and k are constants. The constant k is used as a measure of the plasticity of the fibres and values ranging from -3×10^{-5} sec^{-1} have been recorded.

Pulled wool: Wool that is removed from the skins of slaughtered sheep by means of a depilatory, "sweating," or some other process.

Quality: This term is used to designate the fineness of wool fibres. The quality is given in the American or Bradford Systems by applying to wool of a certain degree of fineness the corresponding accepted term; such as, half blood, or 60's Quality is sometimes used in referring to strength and colour.

Raw wool: Wool in the grease.

Regain: The perdentage increase in weight due to the moisture, compared with the moisture-free weight. It also means the amount of moisture that wool or a fabric will naturally absorb from the air with a certain relative humidity.

Robust: An Australian term used to describe Merino wool that is relatively coarse compared with other Merino wools. Also called strong. Merino wool may be fine, medium, or strong.

Run-out fleece: Wool that is very lacking in uniformity, being hairy or kempy in the breech or elsewhere.

Scouring (scoured, scoured basis). The process by which the grease and dirt are removed from wool, usually through the use of a warm solution of soap and sodium carbonate, or by means of a solvent such as naphta. After the process, wool is spoken of as scoured, and trading either before or after may be on a clean or scoured basis.

Setting: The ability of keratin fibres to assume a more or less permanent change in shape or length when steamed under stress been exploited.

Semi-bright: Wool that lacks brightness due to the environment under which produced. It is as white as other wool after scouring.

Serrations: The outer scales of the wool fibres show irregular saw-tooth edges called serrations. Visible under a microscope.

Shafty: Wool that is well grown, strong, and of good length for its grade.

Shearlings: Pelts of slaughtered sheep that have been recently shorn and have less than about an inch of wool. Also, wool pulled from such pelts. Also, as English term for a yearling sheep.

Shoddy: Wool fibres recovered from old or new woven rags.

Shrinkage: The percentage loss in weight due to scouring.

Skirting (skirted) Removing the inferior and heavy shrinking parts of a fleece before it is packed for sale. Commonly practiced in Australia and many other countries.

Slipes (slipe wool) British term for pulled wool.

Sound (soundness). Wool that has good strength.

Spinning count or counts: A numerical system of wool grading on the basis of the number of hanks of yarn that can be spun from it. The count indicates the number of hanks each of 560 yards that it will take to weigh a pound.

Spring wool: Wool shorn in the spring in contrast with fall wool where sheep are shorn twice a year. It is preferred to fall wool as it is longer stapled.

Stained wool: Wool that has been stained by urine or otherwise so that it cannot be scoured to a pure white colour. Subject to price discount.

Staple: Now commonly used in reference to length of wool fibres. It is measured without stretching to remove the crimp which would give the fibre length.

Staple also means a lock or bunch of wool fibres as they exist in the fleece.

Stabble (stabble shearing). Shearing a short distance from the skin. Usual with show sheep.

Suint: The water-soluble perspiration naturally found in a fleece. It is mixed with the yolk.

Sweating process: Piling sheep skins in a warm, moist room to loosen the wool for pulling.

Tags: The heavy manure-covered locks.

Tare: The weight of the wool sacks deducted before payment is made for the wool.

Tender: Wool that is weak and breaks easily. Tender wool is usually due to poor nutrition or sickness.

Tippy wool: That in which the tip or weather end of the fibres are encrusted, making the wool wasty in processing.

Top: A strand of partially manufactured wool. It has been scoured and combed, and the fibres lie parallel in the strand. Wool in this form is ready to be drawn and spun and is a standard commercial article and is dealt in on the futures market.

Unwashed: Wool in the grease.

Virgin wool: That which has been used in fabrics for the first time in contrast with wool that may be called all wool or pure wool but which has been recovered from previously made materials.

Warp: The threads of a fabric that run lengthwise. They must be strong to withstand the strains of weaving.

Washed wool: Wool from sheep washed before they were shorn. Another out-of-date practice in U.S.A. but followed to some extent in England.

Weft: The opposite of warp. See filling.

Wool fat(grease): See degras and lanolin.

Worsteds: Fabrics made from combed wool.

Yield: The opposite of shrinkage. The percentage of clean wool fibres after scouring.

Yield Point: The straight part of the curve gives way to a bend and beyond this point, or region, the material no longer behaves like a spring or elastic. Large extensions are produced by relatively small increases in the stress and most of the stretch in irrecoverable. This bending of yield region is located by the yield point, which is determined geometrically. The point at which the tangent to the curve is parallel to the line joining the origin and the breaking point is taken as the yield point.

Hence, the yield point may be defined in terms of the yield stress and the yield strains.

Yolk: The secretion of sebaceous or oil glands in the skin. A certain amount is needed to keep the wool in good condition.

Work of Rupture: It is the energy or work required to break the specimen The arc under load-elongation curve, represents the work done in stretching the specimen to breaking point. Units of the work of rupture will be in units of work, e.g. gram-centimeter or grams per denier.

Elastic recovery: It is defined as that property of a fibre by which it tends to recover its original size and shape after deformation. It is expressed as:-

$$= \frac{\text{elastic extension}}{\text{Total extension}}$$

Load: The application of a load to a fibre in its axial direction causes a tension to be developed in the specimen. The load is usually expressed in grams weight or pounds weight.

Stress: It is the ratio between the force applied and the cross-section of the specimen.

Mass Stress: It is the ratio of the force applied to the linear density (Mas per unit length.) Unit of mass stress is grams weight per denier or grams weight per tex.

Tenacity or specific strength: It is the mass stress at break the units being same as the mass stress.

Strain: It is the ratio of elongation to initial length

$$\text{Strain} = \frac{\text{Elongation}}{\text{Initial length}}$$

Extension: By expressing the strain as a percentage we get the extension.

$$\text{Extension} = \frac{\text{Elongation}}{\text{initial length}} \times 100 \text{ percent}$$

Denier: It is the linear density expressed as the mass in grams of 9,000 metres of fibre.

Tex: It is the weight in grams of 1 K m of yarn.

Resilence: Is the springiness of a fibre mass, or ability of a fibre to come back to its original volume after being compressed. This property is desired to a high degree in carpet work.

Rigidity: The rigidity of the wool fibre is the property which determines its resistance to the insertion of twist, and is, therefore of great interest in spinning.

APPENDIX 2

Birefringence Measurement

Birefringence can be useful to estimate the degree of order as it provides a measure of the orientations of the Structural Units comprising the wool. When allowance is made for swelling, the birefringence of wool is essentially independent of moisture content.

The measurement of birefringence will also reveal the alignment along the axis. For this reason, it is a useful measurement of the presence of disorder. It is considerably reduced by any disorganisation. For native keratins the values are the order of 1.0×10^{-2}. The other values are as under:

Costwold Wool

Temperature	Humidity	Birefringence
22°C	65%	11×10^{-3}
22°C	100%	9.2×10^{-3}
		$\simeq 9.5 \times 10^{-3}$

Method:

A Snippt, about 5 cm. in length was cut from the middle region of each variety of wool fibre. Birefringence and diameter measurements were both made on the same portion of snippt, immersed in benzene, at four regularly spaced intervals along its length.

The Senarmont method is applied in measuring the birefringence. The purpose of the Senarmont method is to determine the parameters of elliptically polarised-light, and thus allow to calculate the phase difference between the components, from which the path difference and hence the birefringence of a material can be computed (3,4,5,6).

Calculation of Birefringence.

If θ_1 and θ_2 are two different angles when the polarized light appears and then extint, we have, Phase difference = $\theta = \theta_1 - \theta_2$

and birefringence = $\frac{\theta}{2\pi} \left(\frac{\lambda}{d}\right)$

$$= \frac{2\theta}{360} \cdot \frac{\lambda}{d}$$

where λ is the wavelength of the light used (sodium light in this case λ = 5890 A). Hence Birefringence = $B = 3.27 \times 10^{-3} \times \frac{\theta}{d}$

Comments.

The birefringence of pure wools as well as the wool treated with M^{2+} ion, have been measured. The results are tabulated on next page.

From the data it is noted that birefringence is increased when they are treated with cations (M^{2+}), which is not unexpected. As stated earlier, there is possibility of disorganisation and orientation due to stretching of NH and C=O bonds, in presence of these ions.

There is increase of birefringence for Merino, decrease for Cross and no change for Yankasa.

BIREFRINGENCE OF DIFFERENT WOOLS AT 22°C 65%

Wool	Mean diameter (μm)	Angle	Birefringence
Merino	27.44	148°	17.64×10^{-3}
Cross	26.95	156	18.93×10^{-3}
Yankasa	193.5	135	2.28×10^{-3}
Baluchi	39.2	85.0	7.09×10^{-3}
Wensleydale	46.55	120	8.43×10^{-3}

Table BIREFRINGENCE DATA FOR DIFFERENT WOOLS

At. Temperature 22°C.

Wool	Pure Wool			0.33 $NnCl_2$			0.33 $NiCl_2$			033 $CoCl_2$			0.33 $MnCl_2$		
	Mean dia µm	Angle θ° (mean)	Biref x 10^{-3}	Mean dia µm	Angle θ° (mean)	Biref x 10^{-3}	Mean dia µm	Angle θ° (mean	Biref x 10^{-3}	Mean dia µm	Angle θ° (mean)	Biref x $a0^{-3}$	Mean dia µm	Angle θ° (mean)	Biref. x 10^{-3}
Merino	27.5	147	17.48	26.4	160	19.82	23.3	156	21.89	23.10	165	23.36	27.5	145	17.24
Cross	19.8	164	27.08	28.0	147	17.17	28.0	110	12.85	24.0	138	18.80	22	147	21.85
Yankasa	193.5	135	2.28	209.33	137	2.14	206.57	137	2.169	208.5	139	2.18	195.9	133	2.22

NOTE: B(Birefringence) = $(\phi/2\Pi)(\lambda/d) = \frac{2\theta^{o}}{360} \times \frac{\lambda}{d} = 3.27 \times 10^{-3} \frac{\theta}{d}$

where θ = Phase difference

λ = wavelength of light (Sodium light = 5890°A)

d = diameter of wool

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APPENDIX 3

TABLE NO.1

ACID TITRATION DATA FOR MERINO WOOL

AT TEMP.= 25°C.

1.00g of MERINO WOOL + HCl

No Salt Added.

NO	VOL OF HCl (Cm^3)	APPROX CONCN OF HCl	CONCN OF HCl		pH OF THE SOLUTION		milli-moles OF HCl/100g OF MERINO WOOL
			Initial	Final	Initial	Final	
1	70	0.8M	0.8	0.79		0.1	83.34
2	70	0.5M	0.099	0.0895		1.05	79.34
3	70	0.10M	0.1035		0.985	1.02	65.98
4	70	0.02M			1.85	1.87	54.17
5	50	0.03M			2.10	2.50	28.45
6	50	0.032M			2.26	2.80	23.00
7	50	0.035M			2.56	3.25	13.00
8	50	0.04M			2.66	3.66	11.7
9	50	0.05M			2.80	4.60	9.3
10	50	0.001M			3.14	6.30	4.3
11	50	0.0001M			4.00	6.45	0.6

TABLE NO.2

ACID TITRATION DATA FOR MERINO WOOL AT TEMP. = 25°C

1.00g of MERINO WOOL + HCL + 0.1M NaCl

NO.	VOL. OF HCl (Cm^3)	APPROX. CONCN OF HCL	CONCN. OF HCl	pH OF THE SOLUTION			milli-moles OF HCl/100g OF MERINO WOOL
			Initial	Final	Initial	Final	
1	50	1.0M	0.94	0.925		0.034	89.32
2	50	0.3M	0.282	0.277		0.55	76.90
3	50	0.1M	0.0856	0.0756		1.141	59.29
4	50	0.11M			1.9	2.30	45.107
5	50	0.05M			2.00	2.76	49.18
6	50	0.04M			2.20	3.40	35.19
7	50	0.03M			2.18	2.8	29.90
8	50	.02M			2.30	3.30	26.85
9	50	.019M			2.52	4.14	17.55
10	50	.018M			2.60	4.12	14.50
11	50	.015M			2.60	5.00	14.88
12	50	.00M			2.9	6.12	7.49

TABLE NO.3

ACID TITRATION DATA FOR MERINO WOOL
AT TEMP. 25°C.
1.00g. of MERINO WOOL + HCl +1.0M NaCl.

NO	VOL OF HCl_3 (Cm^3)	APPROX CONCN OF HCl	CONCN. OF HCl		pH OF THE SOLUTION		milli-moles OF HCl/100g MERINO WOOL
			Initial	Final	Initial	Final	
1	50	0.25M	0.210	0.195		0.710	89.30
2	50	0.2M	0.1015	0.087		1.061	86.32
3	50	0.1M	0.077	0.0635		1.197	80.35
4	50	0.05M			1.67	2.01	67.67
5	50	0.02M			1.80	2.29	63.81
6	50	0.02M			2.00	2.93	52.55
7	50	0.01M			2.37	4.50	25.20
8	50	0.005M			3.30	5.925	23.34
9	50	0.003M			3.50	6.00	4.00

TABLE NO. 4

ACID TITRATION DATA FOR CROSS WOOL

AT TEMP.= 25°C

1.00g of CROSS WOOL + HCl.

NO SALT ADDED.

VOL. OF HCl (CM^3)	APPROX CONCN HCl	Concentration OF HCl		pH of THE SOLUTION		milli-moles OF HCl/100g OF CROSS WOOL
		Initial	Final	Initial	Final	
50	1.0M	0.80	0.785		0.105	88.22
50	0.3M	0.232	0.2168		0.664	87.10
50	0.1M	0.098	0.0841		1.075	81.55
50	0.09M			1.26	1.36	66.48
50	0.08M			1.772	2.00	41.08
50	0.07M			2.06	2.47	33.73
50	0.06M			2.00	2.52	30.05
50	0.05M			2.42	3.14	18.10
50	0.04M			2.47	3.24	16.55
50	0.01M			2.94	4.31	6.44
50	.009 M			3.30	6.32	2.34

TABLE NO.5

ACID TITRATION DATA FOR CROSS WOOL

AT TEMP. = 25°C

1.00g of CROSS WOOL + HCl + .1M NaCl

NO.	VOL. OF HCl_3 (Cm^3)	APPROX CONCN OF HCl	CONCENTRATION OF HCl		pH OF THE SOLUTION		milli-moles OF HCl/100g OF CROSS WOOL
			INITIAL	FINAL	INITIAL	FINAL	
1	50	0.4M	0.35	0.335		0.475	88.24
2	50	0.09M	0.063	0.049		1.31	82.17
3	50	.03M	0.023	0.107		1.96	72.13
4	50	.06M			1.80	1.96	72.13
5	50	.05M			2.32	3.78	32.87
6	50	.03M			2.50	4.47	18.41
7	50	.02M			2.61	4.99	14.38
8	50	.01M			2.70	5.45	9.71
9	50	.001M			4.825	5.90	0.082

TABLE NO.6

ACID TITRATION DATA FOR CROSS WOOL

AT TEMP = 25°C

1.00g of CROSS WOOL + HCl + 1.0M NaCl.

NO.	VOL. OF HCl (Cm^3)	APP CONCN OF	CONCENTRATION OF HCl		pH OF THE SOLUTION		milli-moles OF HCl/100g OF CROSS WOOL
			Initial	Final	Initial	Final	
1	50	0.6M	0.405	0.395		0.4034	102.7
2	50	0.1M	0.074	0.059		1.229	88.24
3	50	0.09M			1.48	1.53	79.41
4	50	0.08M			1.98	2.20	71.20
5	50	0.05M			2.06	3.62	52.24
6	50	0.04M			2.22	4.25	35.12
7	50	0.03M			2.37	4.56	24.93
8	50	0.02M			2.56	4.88	16.12
9	50	0.01M			2.75	5.46	10.44
10	50	0.009M			2.06	3.60	49.94
11.	50	0.008M			2.37	4.75	25.00
12	50	0.007M			3.00	5.90	5.875
13	50	0.005M			3.3	6.0	2.94
14	50	0.003M			3.63	6.3	1.38

Table No. 7

ACID-TITRATION YANKASA WOOL

1.00g of Yankasa wool + 50Cm^3 HCl. No salt added

No.	Volume of HCl	Approx. concn. of HCl	Concentration of solution		pH of solution		Milli-moles of HCl/100g of Yankasa wool
			Initial	Final	Initial	Final	
1.	50	0.9	0.805	0.78		0.11	89.3
2.	50	0.5	0.50	0.486		0.31	85.72
3.	50	0.1	0.09	0.086		1.06	83.33
4.	50	.03	0.02	0.009		2.05	65.45
5.	50	0.02			2.12	2.92	38.00
6.	50	0.01			2.26	3.62	30.41
7.	50	0.005			2.40	5.22	23.67
8.	50	0.003			2.56	5.58	13.01
9.	50	0.002			2.71	6.10	10.57
10.	50	.001			2.80	6.28	9.43
11.	50	.0009			3.00	6.30	5.923

Table No. 8

ACID TITRATION DATA FOR YANKASA WOOL AT TEMP. 25°C

1.00g of Yankasa Wool + HCl + 0.1M NaCl

Vol. of HCl_3 (Cm^3)	Approx. Concn. of HCl	Concentration of HCl		pH of the solution		milli-moles of HCl/100g. of Yankasa wool
		Initial	Final	Initial	Final	
50	0.3					
50	0.2			0.265	0.28	89.3
50	0.1			. / .	0.793	83.33
50	0.09			1.92	2.885	63.70
50	0.08			2.14	3.52	53.22
50	0.07			1.90	2.38	50.125
50	0.06			2.18	3.26	36.055
50	0.05			2.265	4.425	32.11
50	0.04			2.3	4.14	29.40
50	0.03			2.60	4.82	14.86
50	0.02			2.66	5.66	12.92
50	0.01			2.70	5.30	11.845
50	0.005			3.305	5.925	2.34

Table No. 9

TITRATION DATA FOR YANKASA WOOL

AT TEMP = 25°C

1.00g of Yankasa Wool + HCl + 1.OM NaCl

Vol. of HCl_3 (Cm^3)	Approx. Conen. of HCl	Concentration of HCl		pH of the solution		Milli-moles of HCl/100g of Yankasa wool
		Initial	Final	Initial	Final	
50	0.30 M	0.25	0.2345		0.6299	90.15
50	0.25 //	0.21	0.195		0.71	89.30
50	0.025 //	0.021	0.0063		2.200	83.09
50	0.02 //	0.018	0.0045		2.75	80.35
50	0.01 //			1.92	3.75	70.47
50	0.009 //			2.00	4.64	56.75
50	0.008 //			2.30	5.45	37.97
50	0.006 //			2.37	5.04	22.07
50	0.002 //			3.56	6.16	1.87
50	0.001 //			3.30	6.20	2.98

Table No. 10

ALKALI TITRATION

MERINO WOOL AT TEMP = 25°C

1.00g of Merino Wool + 50 Cm^3 NaOH.

NO SALT ADDED

No.	Approx. Conon. of NaOH	Concentration of NaOH		pH of the Solution		Milli-moles of NaOH/100g of wool.
		Initial	Final	Initial	Final	
1	0.16 M	0.096	0.08		12.903	95.23
2	0.05 //	0.052	0.038		12.58	83.33
3	0.02 //	0.0213	0.0174		12.24	82.73
4	0.01 //	0.0091	.00525		11.73	23.21
5	0.05 //	.00465	.00235		11.37	13.64
6	.001 //			10.6	8.96	2.256
7	.005 //			10.42	8.34	1.55
8	.0001 //			9.80	8.18	0.36
9	.00001 //			8.9	7.9	0.043

Table No. 11

ALKALI TITRATION

MERINO WOOL AT TEMP = 25 °C

1.00g of Wool + 50 Cm^3 NaOH + 0.1M. NaCl

No.	Approx. Concn. of NaOH	Concentration of NaOH		pH of the Solution		milli-moles of NaOH/100g of Merino wool
		Initial	Final	Initial	Final	
1	0.8 M	.06746	0.05129		12.71	95.16
2	0.05 "	0.0484	0.0331		12.52	90.01
3	0.04 "	0.0338	0.01995		12.30	81.52
4	.03 "	0.028	0.01585		12.20	71.31
5	.0035 "	.0064	0.007943		11.9	49.09
6	.003 "			11.56	10.66	19.14
7	.002 "			11.43	10.22	15.24
8	.001 "			11.05	9.00	6.61
9	.0006 "			10.72	8.32	3.12
10	.00004 "			9.55	7.30	0.21
11				9.51	7.27	0.195

Table No. 12

ALKALI TITRATION

MERINO WOOL AT TEMP = 25°C

1.00g of Merino Wool + 50 Cm^3 NaOH + 1.0M NaCl

No.	Approx. Concn. of NaOH	Concentration of NaOH		ph of the Solution		Milli-moles of NaOH of Merino Wool
		Initial	Final	Initial	Final	
1	0.27 M	0.2655	0.245		13.385	104.3
2	0.035 "	0.03495	0.01995		12.30	89.32
3	0.02 "	0.0188	0.01738		12.24	80.80
4	0.025 "	0.026	0.015		12.18	66.02
5	0.02 "	0.0203	.0105		12.02	58.43
6	0.015 "	.001685	.0083	.	11.92	50.8
7	.005 "	.0054	.0024	11.73	11.38	32.01
8	.004 "		. .	11.68	10.78	25.12
9	.003 "			11.42	10.01	16.35
10	.002 "			11.0	9.41	10.18
11	.001 "			11.1	8.8	7.00
12	.005 "			10.83	8.2	4.01
13	.0001 "			9.6	7.9	1.58
14				9.4	6.9	0.15
15				6.7	6.4	0.0001

Table No. 13

ALKALI TITRATION

CROSS WOOL AT TEMP = 25°C

1.00g of Cross Wool + 50 Cm^3 NaOH No salt added

No.	Approx. Concen. of NaOH	Concentration of NaOH		pH of the Solution		Milli-moles of NaOH/ 100g of wool
		Initial	Final	Initial	Final	
1	0.15 N	0.171	0.15		13.18	105.7
2	0.08 "	0.061	0.0455		12.66	91.18
3	0.05 "	0.0475	0.0335		12.525	82.35
4	0.045 "	0.04525	0.0315		12.498	80.99
5	0.030 "	0.0295	0.0175		12.243	70.60
6	0.025 "	0.0015	.0077		11.875	42.65
7	0.010 "	0.0058	.00245		11.38	19.70
8	0.005 "			11.08	9.7	6.77
9	0.0025 "			10.68	8.47	2.8
10	0.001 "			10.20	7.69	0.93
11	0.00075 "			9.96	7.46	0.53
12	0.0005 "			9.16	7.28	0.08

Table No. 14

ALKALI TITRATION

CROSS WOOL AT TEMP = 25°C

1.00g of Cross Wool + 50 Cm^3 NaOH + 0.1M NaCl

No.	Approx. Concn. of NaOH	Concentration of NaOH		pH of the Solution		Milli-moles of NaOH/100g Cross Wool
		Initial	Final	Initial	Final	
1	0.25M	0.226	0.203		13.31	135.3
2	0.15M	0.136	0.1165		13.11	114.7
3	0.08M	0.715	0.056		12.75	91.18
4	0.075M	0.07	0.053		12.72	97.08
5	0.04M	0.037	0.0235		12.37	79.41
6	0.025M	0.0183	0.008		11.90	60.58
7	0.01M	0.0098	0.0065		11.81	37.95
8	.001 M	0.004	.0008-		10.9	18.98
9				10.96	10.16	4.515
10	0.0005			10.92	9.7	4.598
11	0.0004			10.62	8.06	2.45
12	0.0003			10.3	7.2	1.172
13	0.0001			9.95	7.10	0.524

Table No. 15

ALKALI TITRATION CROSS WOOL

AT TEMP = 25°C

1.00g of Cross Wool + 50 Cm^3 NaOH + 1.0M NaCl

No.	Approx. Conon. of NaOH	Concentration of NaOH		pH of the Solution		Milli-moles of NaOH/100g of Cross wool
		Initial	Final	Initial	Final	
1	0.1M	0.096	0.0755		12.88	120.6
2	0.09M	0.085	0.065		12.81	115.0
3	0.08M	0.0778	0.0585		12.77	113.2
4	0.07M	0.069	0.051		12.71	105.2
5	0.05M	0.048	0.0303		12.49	102.9
6	0.04M	0.039	0.0228		12.357	95.61
7	0.03M	0.029	0.0143		12.103	86.78
8	0.02M	0.0188	0.0073		11.86	67.66
9	0.01M	0.0098	0.0025		11.398	42.60
10	.005M			11.18	9.6	8.42
11	.003M			11.02	9.0	6.02
12	.002M			10.77	8.66	5.192
13	.001M			10.99	8.9	5.83
14	.0009 M			10.92	8.5	4.9
15	0.0008 M			10.90	8.1	4.78
16	.0004 M			10.60	7.5	2.37
17	0.0001 M			9.75	7.2	0.134

Table No. 16

ALKALI TITRATION YANKASA WOOL

AT TEMP = 25°C

100g of Yankasa Wool + 50 Cm^3 NaOH. No salt added

No.	Approx. Concn. of NaOH	Concentration of NaOH		pH of the Solution		Milli-moles of NaOH/100g of wool
		Initial	Final	Initial	Final	
1	0.10M	0.096	0.08		12.903	95.23
2	0.06M	0.052	0.0405		12.61	68.45
3	0.03M	0.0211	0.0136		12.134	44.65
4	0.01M	0.0091	0.0051		11.71	23.81
5	0.008 M	0.005	0.0019		11.28	16.25
6	0.001 M			10.78	8.02	2.363
7	.00075 M			10.42	7.68	1.563
8	.0005 M			9.68	7.55	0.283
9	.00001 M			8.7	7.0	0.026

Table No. 17

ALKALI TITRATION YANKASA WOOL

AT TEMP = 25°C

100g of Yankasa Wool + 50 Cm^3 NaOH + 0.1M NaCl

No.	Approx. Concn. of NaOH	Concentration of NaOH sol.		pH of the Solution		Milli-moles of NaOH/100g of wool
		Initial	Final	Initial	Final	
1	0.06 M	.058	0.00435		12.638	86.56
2	0.05 "	0.05	0.037		12.57	79.18
3	0.04 "	0.036	0.026		12.40	59.48
4	0.03 "	0.028	0.0185		12.26	56.54
5	0.02 "	0.020	.0012		12.07	49.29
6	0.01 "	0.0051		11.71	10.6	28.14
7	0.0001 "			10.88	8.46	4.5
8	0.00005 "			10.6	7.88	0.85
9	0.00001 "			10.15	7.00	0.148

Table No. 18

ALKALI TITRATION YANKASA WOOL

AT TEMP = 25°C

1.00g of Yankasa Wool + 50 Cm^3 NaOH + 1.0M NaCl

No.	Approx. Concn. of NaOH	Concentration of NaOH sol.		pH of the Solution		Milli-moles of NaOH/100g of wool
		Initial	Final	Initial	Final	
1	0.3 M	0.265	0.25		13.39	89.32
2	0.2 "	0.175	0.165		13.217	59.98
3	0.05 "	0.073	0.064		12.81	53.60
4	0.045 "			11.15	10.9	37.42
5	0.043 "			11.76	10.5	32.37
6	0.040 "			11.46	10.4	15.67
7	0.030 "			11.23	9.22	9.815
8	0.025 "			11.12	8.66	7.82
9	0.010 "			10.93	8.46	5.12
10	0.005 "			10.01	8.00	0.59
11	0.001 "			9.40	7.28	0.15
12	0.00001 "			9.2	6.70	0.09

TABLE NO. 19

TITRATION DATA FOR MERINO WOOL

1.00 g MERINO WOOL ± M/3 $ZnCl_2$ SOLUTION
HCl (M/I) AT TEMPERATURE 25°C
IONIC STRENGTH. (μ) = 1.0

No.	VOLUME OF HCL ADDED Cm^3	CONCN. OF HCl	VOL. OF $ZnCl_2$ (M/S) Cm^3	pH OF THE SOLUTION		Milli-moles of HCl/100 g of Merino Wool
				INITIAL	FINAL	
1	0.01	M/I	100	3.9	4.41	0.87
2	0.02	M/I	100	3.54	4.39	2.28
3	0.03	M/I	100	3.42	4.29	3.20
4	0.05	M/I	100	3.33	4.17	4.10
5	0.08	M/I	100	3.20	4.02	6.40
6	0.3	M/I	100	2.59	3.58	22.9
7	0.4	M/I	100	2.30	3.42	46.3
8	0.5	M/I	100	2.18	3.05	57.2
9	0.6	M/I	100	2.10	2.75	61.6
10	0.7	M/I	100	2.05	2.60	64.0
11	0.8	M/I	100	2.00	2.50	68.0
12	1.5	M/I	100	1.78	2.03	73.0
13	2.0	M/I	100	1.65	1.89	96.9
14	2.5	M/I	100	1.57	1.78	103.3
15	2.5	M/I	100	1.52	1.70	103.8

TABLE NO 20

TITRATIO N DATA FOR MERINO WOOL

M/3 $MnCl_2$ Solution

1.00g of Wool + $MnCl_2$ + HCl. (M/I)

at temperature = 25°C, IONIC STRENGTH(μ) = 1.0

No.	Vol. of HCl added cm^3	Concn. of HCl	Vol. of $MnCl_2$ M/3 cm^3	pH of the Solution		milli-moles of HCl per 100 g. of wool.
				Initial	Final	
1	0.01	M/1	100	4.21	5.34	. 0.57
2	0.02	M/1	100	3.87	5.31	. 1.30
3	0.03	M/1	100	3.69	5.20	2.00
4	0.05	M/1	100	3.54	5.16	2.90
5	0.08	M/1	100	3.51	4.83	4.70
6	0.10	M/1	100	3.28	4.74	9.80
7	0.30	M/1	100	2.58	3.70	26.80
8	0.40	M/1	100	2.49	3.18	31.4
9	0.50	M/1	100	2.28	2.82	35.00
10	0.60	M/1	100	2.20	2.62	39.10
11	1.0	M/1	100	2.01	2.35	54.5
12	1.5	M/1	100	1.81	2.10	76.3
13	2.0	M/1	100	1.71	1.95	84.5
14	2.5	M/1	100	1.65	1.83	88.0
15	3.0	M/1	100	1.38	1.63	102.3

TABLE NO. 21

TITRATION DATA FOR MERINO WOOL

M/3 Nickel Chloride Solution

1.00 g of wool + $NiCl_2$ + HCl (M/1)

at temperature 25°C, IONIC STRENGTH (μ) = 1.0

No.	Volume of HCl (cm^3)	Concn. of HCl added	Volume of $NiCl_2$ M/3 cm^3	pH of the solution		milli-moles of HCl per 100 g of wool
				initial	final	
1.	0.05	M/1	100	5.10	5.49	0.06
2.	0.07	M/1	100	4.37	5.21	0.37
3.	0.1	M/1	100	5.3	5.2	11.2
4.	0.2	M/1	100	4.78	4.72	19.8
5.	0.3	M/1	100	4.16	4.48	31.3
6.	0.4	M/1	100	3.94	4.18	39.1
7.	0.5	M/1	100	3.25	3.80	40.1
8.	0.6	M/1	100	3.00	3.45	48.9
9.	0.8	M/1	100	2.70	3.08	57.8
10.	2.0	M/1	100	1.86	2.20	74.9
11.	2.5	M/1	100	1.73	2.06	89.1
12.	3.0	M/1	100	1.64	1.99	126.8
13.	3.1	M/1	100	1.37	1.50	130.0

TABLE NO. 22

TITRATION DATA FOR MERINO WOOL

1.00 g MERINO WOOL ≡ M/3 cobalt cloride Solution

HCl (M/I) AT TEMPERATURE 25°C

IONIC STRENGTH 1.0

No.	VOLUME OF HCl ADDED (Cm^3)	CONCN. OF HCl	VOL. OF $CoCl_2$ (M/3) Cm^3	pH OF THE SOLUTION		Milli-moles of HCl/100 g of Merino Wool
				INITIAL	FINAL	
1	0.05	M/	100	5.40	5.59	0.14
2	0.10	M/I	100	3.04	5.23	9.10
3	0.2	M/I	100	2.75	4.76	17.60
4	0.3	M/I	100	2.59	4.34	25.2
5	0.4	M/I	100	2.37	3.68	33.8
6	0.5	M/I	100	2.37	3.68	40.6
7	0.6	M/I	100	2.28	3.41	48.6
8	0.7	M/I	100	2.23	3.11	51.1
9	0.8	M/I	100	2.15	3.01	61.0
10	0.9	M/I	100	2.0	2.50	68.0
11	1.5	M/I	100	1.7	2.04	74.5
12	2.0	M/I	100	1.50	1.65	92.0
13	2.5	M/I	100	1.01	1.06	106.2

TABLE NO. 23

TITRATION DATA FOR CROSS WOOL

M/3 Zinc cloride SOLUTION

1.00 g Of Cross ~~Wool~~ Wool + 100 Cm^3 $ZnCl_2$ + HCl (M/I)

AT TEMPERATURE 25°C IONIC STRENGTH μ = 1.0

No.	Volume OF HCl ADDED Cm^3	Concn. OF HCl	pH OF THE SOLUTION		Milli-Moles of HCl/ 100 g of CROSS WOOL
			INITIAL	FINAL	
1	0.01	M/10	3.32	5.3	4.71
2	0.05	M/10	3.10	5.01	7.80
3	0.08	M/10	3.00	4.72	9.8
4	0.10	M/10	2.95	4.75	11.1
5	0.15	M/10	2.92	4.73	11.8
6	0.20	M/10	2.88	4.70	13.0
7	0.30	M/10	2.875	4.67	13.1
8	0.40	M/10	2.82	4.61	14.9
9	0.50	M/10	2.79	4.51	15.9
10	0.10	M/1	2.75	4.58	17.5
11	0.20	M/1	2.60	4.38	24.7
12	0.30	M/1	2.415	3.96	37.4
13	0.50	M/1	2.29	3.69	47.1
14	1.0	M/1	2.10	2.63	56.0
15.	1.5	M/1	1.78	2.03	73.8
16	2.0	M/1	1.52	1.69	98.1
17	2.5	M/1	1.15	1.22	98.6
18	3.0	M/1	1.14	1.01	99.8
19	3.5	M/1		0.92	100.1

TABLE NO. 24

TITRATION DATA FOR CROSS WOOL

M/3 Manganese chloride SOLUTION

1.00 g Of Cross Wool + 100 Cm^3 $MnCl_2$ + HCl (M/1)

AT TEMPERATURE 25°C IONIC STRENGTH, μ = 1.0

NO.	VOLUME OF HCl ADDED Cm^3	Concn. OF HCl	pH OF THE SOLUTION		Milli-moles OF HCl 100 g OF CROSS WOOL
			INITIAL	FINAL	
1	0.05	M/10	4.11	6.50	0.8
2	0.8	M/10	3.73	6.31	1.9
3	0.1	M/10	3.32	5.93	4.8
4	0.15	M/10	2.79	5.43	10.35
5	0.20	M/10	2.63	4.99	23.30
6	0.3	M/10	2.28	4.10	51.7
7	0.4	M/10	2.18	3.64	63.8
8	0.5	M/10	2.00	2.73	82.0
9	0.1	M/1	1.90	2.47	93.3
10	0.2	M/1	1.69	1.99	103.0
11	0.5	M/1	1.57	1.78	106.0
12	1.0	M/1	1.38	1.53	122.5
13	1.5	M/1	?	1.200	124.3 ?
14	2.0	M/1	?	1.01	125.1 ?
15	2.5	M/1	?	0.90	125.9 ?

TABLE NO. 25

ACID TITRATION DATA FOR CROSS WOOL

M/3 Nickel Chloride SOLUTION

1.00 g of Cross Wool + 100 Cm^3 $NiCl_2$ + HCl (M/1)

AT TEMPERATURE 25°C. IONIC STRENGTH, = 1.0

NO	VOLUME OF HCl Added (CM^3)	CONCN. OF HCl	pH OF THE SOLUTION		milli-moles OF HCl/100g CROSS WOOL
			Initial	Final	
1	0	-	5.74	5.76	0.06
2	0.1	M/10	3.73	5.69	1.84
3	0.15	M/10	3.615	5.66	2.41
4	0.2	M/10	3.49	5.60	3.21
5	[illegible]	M/10	[illegible]	[illegible]	[illegible]
6	0.1	M/1	2.60	4.56	24.9
7	0.2	M/1	2.15	3.47	67.4
8	0.5	M/1	1.86	2.42	100.0
9	1.5	M/1	1.64	1.99	126.0
10	2.0	M/1	1.30	1.40	134.5

TABLE NO. 26

TITRATION DATA FOR CROSS WOOL

M/3 Cobalt Chloride + SOLUTION

I.00 g of Cross Wool + 100 cm^3 $CoCl_2$ HCl (M/I)

AT TEMPERATURE 25°C. IONIC STRENGTH = 1.0

No	Volume OF HCl (CM^3)	CONCN. OF HCl	pH OF THE SOLUTION		milli-moles OF HCl/100g OF CROSS WOOL
			Initial	Final	
1	0.15	M/1	4.095	5.70	0.78
2	0.20	M/1	3.90	5.65	1.30
3	0.5	M/1	3.67	5.52	2.10
4	0.1	M/1	3.09	5.19	8.10
5	0.2	M/1	2.63	4.33	23.1
6	0.3	M/1	2.28	3.70	50.1
7	0.4	M/1	1.95	2.34	66.5
8	0.5	M/1	1.785	2.05	75.9
9	1.0	M/1	1.705	1.99	94.9
10	1.5	M/1	1.35	1.46	98.9
11	2.0	M/1	1.20	1.265	109.0

TABLE NO. 27

TITRATION DATA FOR YANKASA WOOL

M/3 Zinc Chloride Solution

1.00 g of YANKASA WOOL + 100Cm^3 $ZnCl_2$ + HCl., AT TEMPT = 25°C

IONIC STRENGTH (μ) = 1.0

No.	Volume OF HCl Added (Cm^3)	CONCN. OF HCl	pH OF THE SOLUTION		Milli-moles OF HCl/100 g YANKASA WOOL
			Initial	Final	
1	0	-	3.16	5.15	6.84
2	0.02	M/10	3.00	4.755	9.82
3.	0.05	M/10	2.95	4.70	11.02
4	0.10	M/10	2.92	4.65	11.80
5	0.20	M/10	2.88	4.63	12.95
6	0.30	M/10	2.875	4.615	12.94
7	0.40	M/10	2.820	4.55	14.86
8	0.50	M/10	2.79	4.27	15.69
9	0.1	M/1	2.60	4.03	24.2
10	0.2	M/1	2.415	3.89	37.2
11	0.3	M/1	2.29	3.625	49.0
12	0.5	M/1	2.10	3.08	71.1
13	1.0	M/1	1.73	2.025	81.8
14	1.5	M/1	1.57	1.75	91.8
15	2.0	M/1	1.45	1.60	105.6
16	2.5	"	1.175	1,25	107.5

Table No. 28

TITRATION DATA FOR YANKASA WOOL

M/3 Manganese Chloride solution

1.00g of Yankasa Wool + 100(Cm^3) $MnCl_2$ + HCl At Temp. = 25°C

Ionic Strength (μ) = 1.0

No.	Volume of HCl added (Cm^3)	Concen. of HCl	pH of the Solution		Milli-moles of HCl/ 100g of Yankasa Wool
			Initial	Final	
1	0.02	M/10	4.11	5.10	0.7
2	0.05	"	3.73	5.09	1.8
3	0.10	"	3.32	4.92	4.8
4	0.2	"	2.97	4.75	10.55
5	0.3	"	2.63	4.73	23.10
6	0.4	"	2.28	3.86	51.1
7	0.5	"	2.18	3.54	63.2
8	0.1	M/1	2.00	2.815	84.7
9	0.2	"	1.90	2.43	86.7
10	0.5	"	1.69	1.97	98.0
11	1.0	"	1.57	1.765	99.4
12	1.5	"	1.22	1.30	102.4

Table No. 29

TITRATION DATA FOR YANKSA WOOL M/3

Nickel Chloride solution 1.00g of Yankasa Wool
+ 100Cm^3 $NiCl_2$+ HCl A t Temp. = 25°C

Ionic Strength (μ) = 1.0

	Volume of HCl added (Cm^3)	Concn. of HCl	pH of the Solution		Milli-Moles of HCl/100g of Yankasa Wool
			Initial	Final	
1	0	-	5.12	5.22	0.02
2	0.05	M/10	3.905	5.195	1.20
3	0.10	M/10	3.73	5.185	1.80
4	0.15	"	3.615	5.17	2.20
5	0.20	"	3.49	5.15	3.2
6	0.10	M/1	2.895	5.09	12.7
7	0.20	"	2.60	4.75	23.3
8	0.50	"	2.15	4.10	62.8
9	1.0	"	1.86	2.70	118.0
10	1.5	"	1.68	2.10	139.0
11	2.0	"	1.28	1.42	146.5

Table No. 30

TITRATION DATA FOR YANKASA WOOL

M/3 Cobalt Chloride Solution

1.00g of Yankasa Wool + 100 (Cm^3) $MnCl_2$ + HCl At Temp. = 25°C

Ionic Strength (μ) = 1.0

No.	Volume of HCl added (Cm^3)	Concn. of HCl	pH of the Solution		Milli-moles of HCl/100g of Yankasa wool
			Initial	Final	
1	0.01	M/10	5.3	5.39	0.09
2	0.02	"	4.79	5.37	0.12
3	0.05	"	4.38	5.305	0.37
4	0.08	"	4.095	5.30	0.75
5	0.10	"	3.90	5.28	1.24
6	0.20	"	3.67	5.14	1.42
7	0.3	"	3.09	4.47	8.02
8	0.5	"	2.63	4.445	19.9
9	1.0	"	28	3.05	53.2
10	0.15	M/1	1.95	2.40	72.2
11	0.2	"	1.785	2.09	83.0
12	0.5	"	1.705	1.995	96.0
13	1.0	"	1.75	1.78	103.2
14	1.5	"	1.52	1.67	111.0
15	2.0	"	1.29	1.40	146.3

TABLE NO. 31

TITRATION DATA FOR MERINO WOOL.

M/ 30 Zinc chloride SOLUTION

I.0 g of MERINO WOOL + M/30 $ZnCl_2$ (100 Cm^3) +

HCl . IONIC STRENGTH( ) = 0.IO

AT TEMPERATURE. 25°C

No.	Volume of HCl Added (Cm^3)	Concn. of HCl	pH of the SOLUTION		Milli-moles of HCl/100 g. Merino WOOL.
			INITIAL	FINAL	
1	0.04	M/IO	3.53	4.85	2.8
2	0.06	M/IO	3.48	4.805	3.2
3	0.08	M/IO	3.62	4.78	3.4
4.	0.10	M/IO	3.43	4,86	3.5
5	0.20	M/IO	3.33	4.75	4.5
6	0.30	M/IO	3.22	4.68	5.8
7	0.40	M/IO	3.14	4.58	7.0
8	0.50	M/IO	3.09	4.54	9.0
9	0.60	M/IO	3.03	4.48	9.I
10	0.7	M/IO	2.99	4.40	I0.0
11	0.80	M/IO	2.9I	4.32	12.I
12	0.90	M/IO	2.87	4.30	13.3
13	I.0	M/IO	2.84	4.22	17.3
14	I.50	M/IO	2.66	3.94	22.I
15	2.00	M/IO	2.55	3.73	34.3
16	0.3	M/I	2.54	3.68	27,6
17	0.35	M/I	2.47	3.54	33.5
18	0.40	M/I	2.43	3.36	34.7
19	0.50	M/I	2.36	3.06	34.9
20	I.00	M/I	2.I0	2.45	44.2
21	I.5	M/I	1.90	2.10	47.3
22	2.0	M/I	I.77	ᵀ .92	50.5
23	2.5	M/I	I.67	I. 80	56.8
24	3.0	M/I	I.62	I, 75	64.I

Table No. 32

TITRATION DATA FOR MERINO WOOL

M/30 $MnCl_2$ Solution. 1.00g of Merino Wool + M/30 $MnCl_2$ (100 Cm^3) + HCl. Ionic Strength (μ) = 0.10

At Temperature 25°C

No.	Volume of HCl added (Cm^3)	Concn. of HCl	pH of the Solution		Milli-moles of HCl/100g Merino Wool
			Initial	Final	
1	0.05	M/10	4.28	5.54	0.49
2	0.10	"	3.92	5.52	1.20
3	0.20	"	3.62	5.49	2.08
4	0.30	"	3.39	5.34	4.1
5	0.4	"	3.26	5.25	5.5
6	0.5	"	3.16	5.15	6.9
7	0.7	"	3.01	5.22	9.7
8	0.8	"	2.96	5.11	10.2
9	0.9	"	2.91	5.06	11.9
10	1.0	"	2.81	4.88	1[illegible].7
11	1.5	"	2.68	4.44	20.9
12	2.0	"	2.56	4.03	27.2
13	2.5	"	2.48	3.71	32.0
14	3.0	"	2.40	3.44	37.7
15	0.5	"	2.33	3.05	38.5
16	1.0	"	2.08	2.43	45.3
17	1.5	"	1.91	2.13	50.0
18	2.0	"	1.78	1.90	56.8
19	2.5	"	1.68	1.82	59.5
20	3.0	"	1.575	1.70	68.6

Table No. 33

TITRATION DATA FOR MERINO WOOL

1.00g of Merino Wool + M/30 $NiCl_2$ (100 Cm^3) + HCl. Ionic Strength (μ) = 0.10

At Temperature 25°C

No.	Volume of HCl added (Cm^3)	Concn. of HCl	pH of the solution		Milli-Moles of HC/100g Merino wool
			Initial	Final	
1	0.2	M/10	4.54	5.17	0.22
2	0.4	"	3.92	5.06	1.12
3	0.5	"	3.49	4.82	3.10
4	1.0	"	2.855	4.615	13.9
5	1.5	"	2.7	4.23	19.7
6	0.05	"	4.22	5.47	0.57
7	0.10	"	3.97	5.46	1.04
8	0.15	"	3.64	5.36	2.25
9	0.3	M/1	2.60	3.83	24.35
10	0.35	"	2.53	3.64	29.0
11	0.40	"	2.46	3.41	32.0
12	0.45	"	2.41	3.36	35.6
13	0.50	"	2.37	3.17	37.7
14	1.0	"	2.06	2.40	47.4
15	1.5	"	1.89	2.115	58.4
16	2.0	"	1.735	1.920	64.0
17	2.0	M/10	2.58	3.95	25.7
18	2.5	"	2.475	3.70	32.4
19	3.0	"	2.42	3.46	35.6
20	3.5	"	2.34	3.35	42.7

Table No. 34

TITRATION DATA FOR MERINO WOOL

M/30 $CoCl_2$ Solution

1.00g of Merino Wool + M/30 $CoCl_2$ (100 Cm^3) +

HCl. Ionic Strength (μ) = 0.10

At Temperature 25°C

No.	Volume of HCl added (Cm^3)	Concn. of HCl	pH of the Solution		Milli-moles of HCl/100g Merino wool
			Initial	Final	
1	0.40	M/10	4.81	5.15	0.09
2	0.50	"	4.72	5.06	0.10
3	0.60	"	4.68	4.98	0.142
4	0.70	"	4.45	4.85	0.214
5	0.80	"	4.35	4.81	0.30
6	0.90	"	3.12	5.06	7.60
7	1.00	"	3.09	4.95	8.10
8	1.50	"	2.935	4.55	11.60
9	2.00	"	2.82	4.26	14.90
10	2.50	"	2.73	3.96	18.00
11	3.00	"	2.63	3.77	21.50
12	3.50	"	2.56	3.63	25.50
13	0.40	M/1	2.50	3.48	29.50
14	0.45	"	2.45	3.35	32.50
15	0.5	"	2.40	3.22	35.50
16	0.55	"	2.30	3.14	42.90
17	1.0	"	2.065	2.40	46.40
18	1.5	"	1.89	2.08	47.00
19	2.0	"	1.71	1.92	54.60
20	2.50	"	1.675	1.81	57.80
21	3.00	"	1.58	1.70	65.40

TABLE NO.35

ALKALI TITRATION DATA. FOR MERINO WOOL

AT TEMP. = 25°C - IN PRESENCE OF SALT

M/3 Cobalt Chloride solution

1.00g of MERINO WOOL + M/3 $CoCl_2$ Sol ($100cm^3$)
+ M/1 NaOH.

IONIC STRENGTH (M) = 1.0

NO	VOL. OF NaOH (Cm^3)	CONCN OF NaOH	pH OF THE SOLUTION		milli-moles OF NaOH/100g of MERINO WOOL
			INITIAL	FINAL	
1	0.1	M/1	6.80	6.71	0.12
2	0.2	"	6.89	6.81	0.13
3	0.3	"	6.93	6.90	0.06
4	0.4	"	6.96	6.93	0.06
5	0.5	"	6.98	6.96	0.04
6	0.6	"	7.01	6.97	0.17
7	0.7	"	7.09	6.98	0.17
8	0.8	"	7.15	7.01	0.04
9	0.9	"	7.25	7.03	0.07

TABLE NO. 36

ALKALI TITRATION DATA. FOR MERINO WOOL
AT TEMP. = 25 °C . IN PRESENCE OF SALT.

1.00g of MERINO WOOL + M/3 Manganese Chloride $MnCl_2$ (100 cm^3)+ M/1 NaOH.

IONIC STRENGTH (M) = 1.0

NO	VOL. OF NaOH (Cm^3)	CONCN NaCl	pH OF THE SOLUTION		milli-moles OF NaOH/100g of MERINO WOOL.
			INITIAL	FINAL	
1.	0.1	M/1	5.91	6.1	0.17
2	0.2	"	6.50	6.2	0.16
3	0.3	"	6.40	6.3	0.05
4	0.4	"	6.50	6.5	0.0
5	0.5	"	6.7	6.5	0.05
6	0.6	"	6.7	6.5	0.05
7	0.7	"	6.7	6.5	0.05
8	0.8	"			

TABLE NO. 37

ALKALI TITRATION DATA. FOR MERINO WOOL
AT TEMP. = 25°C IN PRESENCE OF SALT
M/3 Zinc Chloride Sol.
1.00g of MERINO WOOL + $\frac{M}{3}$ $ZnCl_2$ Sol ($100Cm^3$)
+ M/1 NaOH
IONIC STRENGTH (M) = 1.0

NO	VOL. OF NaOH (Cm^3)	CONCN OF NaOH	pH of THE SOLUTION		Milli-moles OF NaOH/100g of MERINO
			INITIAL	FINAL	
1	0.1	M/1	5.2	4.60	7.6
2	0.2	"	5.4	5.28	0.61
3	0.3	"	5.5	5.45	0.34
4	0.4	"	5.66	5.50	1.61
5	0.5	"	5.68	5.40	2.39
6	0.6	"	5.70	5.52	1.7
7	0.7	"	5.70	5.58	1.2
8	0.8	"	5.72	5.68	1.3
9	0.9	"	5.9	5.70	2.93

TABLE NO. 3a

ALKALI TITRATION DATA. FOR MERINO WOOL

AT TEMP. = 25°C. IN PRESENCE OF SALT.
M/3 NICKEL CHLORIDE SOLUTION
1.00g of MERINO WOOL + $\frac{M}{3}$ $NiCl_2$ (100 cm^3).
+ M/1 NaOH.
IONIC STRENGTH = 1.0

NO	VOL. OF NaOH (CM^3)	CONCN OF NaOH	pH OF THE SOLUTION		milli-moles OF NaOH/100g of MERINO WOOL.
			INITIAL	FINAL	
1	0.1	M/1	6.85	6.73	0.17
2	0.2	"	6.88	6.84	0.07
3	0.3	"	6.92	6.90	0.04
4	0.4	"	6.9[illegible]	6.92	0
5	0.5	"	6.95	6.94	0.02
6	0.6	"	6.96	6.95	0.02
7	0.7	"	6.98	6.97	.02
8	0.8	"	6.99	6.975	.03
9	0.9				

APPENDIX 4

SWELLING DATA

Table No.39

WATER

Temperature = 22°C.

	Merino: diam. = 18μ			Cross: diam. = 19.2μ			Yankasa: diam. = 188μ		
Time in Minute	Swollen diam. (μ)	% increase of diam. Swelling	% increase of volume Swelling	Swollen diam. (μ)	% increase of diam. Swelling	% increase of volume Swelling	Swollen diam. (μ)	% increase of diam. Swelling	% increase of volume Swelling
1	20.1	11.5	24.3	21.6	12.5	26.6	221.8	18.0	39.2
2	20.1	11.9	25.2	21.6	12.7	27.0	238.8	27.0	61.3
5	20.3	12.75	27.1	21.7	13.0	27.7	258.5	37.5	89.1
10	20.9	16.0	34.6	21.9	14.2	30.4	263.4	40.1	96.1
30	21.0	16.5	35.7	22.0	14.8	31.8	267.2	42.1	101.9
60	21.0	16.8	36.4	22.1	15.3	32.9	268.8	43.0	104.5
120	21.0	16.9	36.7	22.2	15.8	34.1	268.8	43.0	104.5
180	21.1	17.0	36.9	22.3	16.1	34.8	268.8	43.0	104.5

Table No.40

SWELLING DATA

Formic Acid: Temperature = 22°C

A = 95% B = 50%

Time in Minute	Merino: diam = 18μ			Cross: diam = 19.2μ			Yankasa: diam = 188μ		
	Swollen diam μ	% increase of diam.	% increase of volume	Swollen diam. μ	% increase of diam.	% increase of volume	Swollen diam. μ	% increare of diam.	% increase of volume
1	28.62	59.0	152.8	30.91	61.0	159.21	293.28	56.0	143.36
2	28.17	56.5	144.9	30.57	59.2	153.45	300.8	60.0	156.0
5	27.90	55.0	140.3	30.34	58.0	149.64	304.56	62.0	162.44
30	27.72	54.0	137.2	30.43	58.5	151.22	308.696	64.2.	169.62
60	27.63	53.5	135.6	29.95	56.0	143.36	314.9	67.5	180.56
120	27.36	52.0	131.0	29.95	56.0	143.36	317.53	68.9	185.27
180	27.36	52.0	131.0	29.53	55.9	143.05	319.13	69.75	188.15
B. 2	24.17	34.3	80.37	26.11	36.0	84.98	235.0	25.0	56.25
5	24.12	34.0	79.56	25.88	34.8	81.71	236.88	26.0	58.76
30	24.21	34.5	80.90	25.90	34.9	81.98	235.94	25.5	57.50
60	24.21	34.5	80.90	25.88	34.8	81.71	235.94	25.5	57.50
120	24.21	34.5	80.90	25.88	34.9	81.71	235.94	25.5	57.50

Table No.41

SWELLING DATA

Hydrochloric Acid (0.2M) = 0.7%

Temperature = 22°C

Time in Minute	Merino: diam. = 18μ			Cross: diam. = 19.2 μ			Yankasa: diam: = 188 μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume
05	19.53	8.5	17.72	20.93	9.0	18.81	224.66	19.5	40.80
10	19.89	10.6	22.10	21.50	12.0	25.44	258.97	37.75	89.75
30	19.91	10.6	22.32	21.50	12.0	25.44	259.31	37.93	90.25
60	19.91	10.6	22.32	21.50	12.50	25.44	259.35	37.95	95.86
120	19.91	10.6	22.3	21.50	12.0	25.44	259.35	37.95	95.86

Table No. 42

SWELLING DATA

Formamide (Conc. 99%)

Temperature = 22°C

Time in Minute	Merino: diam. = 18.0μ			Cross: diam. = 18.2μ			Yankasa: diam. = 188μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume
5	18.2	1.0	2.0		0	0	-	-	-
10	18.5	2.5	5.1	18.8	3.5	7.1	202.1	7.5	15.6
30	20.0	11.0	23.2	20.5	12.5	26.6	225.1	19.8	43.4
60	20.9	16.0	34.6	21.4	17.8	38.7	227.9	21.2	46.9
120	21.8	21.0	46.4	22.4	23.2	51.7	234.8	24.9	56.0
180	21.8	21.1	46.4	22.4	23.3	51.9	235.2	25.1	56.5
				DIMETHYL FORMAMIDE (Concn.50%					
5	18.4	2.0	4.1	18.8	3.0	6.1	189.9	1.0	2.0
10	18.7	4.0	8.2	19.3	6.0	12.4	192.7	2.5	5.1
30	19.1	5.9	12.1	19.7	8.0	16.6	195.3	3.9	8.0
60	19.4	7.5	15.6	20.0	10.0	21.0	198.9	5.8	11.9
120	19.8	9.75	20.5	20.0	10.0	21.0	201.0	6.9	14.3
180	19.8	9.75	20.5	20.0	10.0	21.0	201.0	6.9	14.3

Table 43

SWELLING DATA

Phenol: 10% Temperature = 22°C

Time in Minute	Merino: diam = 18.0μ			Cross: diam = 18.2μ			Yankasa: diam = 188μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume
5	22.1	23.0	51.3	23.1	27.0	61.3	282.0	50.0	125.0
10	22.5	24.9	56.0	23.1	27.0	61.3	297.0	58.0	149.6
30	22.7	26.0	58.8	23.1	27.0	61.3	338.4	80.0	224.0
60	23.2	29.0	66.4	23.7	30.0	69.0	376.0	100.0	300. 0
120	23.3	29.5	67.7	23.7	30.0	69.0	376.0	100.0	300.0
				(PHENOL) Conen. 90%					
5	21.6	20	44.0	22.9	26.0	58.8	261.3	39	93.2
10	22.5	25	56.3	24.9	37.0	87.7	282.0	50	125.0
30	23.2	29	66.4	27.1	49.0	122.0	325.2	73	199.3
60	24.3	35	82.3	27.3	50.0	125.0	336.5	79	220.4
120	24.5	36	85.0	27.4	50.5	126.5	338.4	80	224.5
180	24.5	36	85.0	27.3	50.0	125.0	338.4	80	224.0

Table 44 SWELLING DATA

(Formaldehyde 40%) Temperature = 22°C

Time in Minute	Merino: diam = 18.0μ			Cross: diam = 18.2μ			Yankasa: diam = 188μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume
5	21.5	20.0	44.0	22.9	26.0	58.8	263.0	39.0	93.2
10	22.5	25.0	56.3	24.9	37.0	87.7	282.0	50.0	125.0
30	23.2	29.0	66.4	27.1	49.0	112.0	304.6	62.0	162.4
60	23.8	32.0	74.2	27.3	50.0	125.0	325.2	73.0	199.3
120	47.3	35.0	82.3	27.5	51.0	128.0	336.5	79.0	220.4
180	47.3	35.0	82.3	27.5	51.0	128.0	338.4	80.0	224.0
				(Acetaldehyde Conc. 100%)					
5	18.2	0	0	18.2	0	0	188	0	0
10	18.3	1.0	2.0	18.2	0	0	188	0	0
30	18.4	1.5	3.0	18.2	0	0	188	0	0
60	18.4	2.0	4.0	18.5	1.5	3.0	191.4	2.1	4.2
120	18.4	2.1	4.2	18.6	1.9	3.8	193.3	2.8	5.7
180	18.4	2.1	4.2	18.7	2.75	5.7	195.5	4.0	8.2

Table 45

SWELLING DATA

Acetic Acid 50% Temperature = 22°C

Time in Minute	Merino: diam = 18.0μ			Cross: diam = 18.2 μ			Yankasa: diam = 18μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	%increase of diam.	% increase of volume
5	27.2	51.0	12.8	27 8	53.0	13.4	27.8	48.0	11.9
10	27.4	52.0	13.1	28.0	54.0	13.7	28.0	48.9	12.2
30	27.5	52.9	13.4	28.2	55.0	14.0	28.2	50.0	12.5
60	27.5	53.0	13.4	28.2	55.0	14.0	28.2	49.8	12.4
120	27.5	53.0	13.4	28.2	55.0	14.0	28.2	50.0	12.5
180	27.5	53.0	13.4	28.2	55.0	14.0	28.2	50.0	12.5
				ACETIC ACID 100%					
10	-	-	-	-	-	-	190.0	1.0	2.0
30	-	-	-	-	-	-	197.4	5.0	10.3
60	-	-	-	-	-	-	198.3	5.5	11.3
120	-	-	-	-	-	-	199.2	6.0	12.4

Table No.46 SWELLING DATA

Urea (50% concentration) Temperature = 22°C

Time in Minute	Merino: diam = 18.0M			Cross: diam = 18.2M			Yankasa diam = 188μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam	% increase of diam.	% increase of volume	Swollen diam	% increase of diam.	% increase of volume
1	18.9	5.6	10.3	19.2	5.6	11.5	188	0	0
5	20.3	12.5	26.6	20.5	12.5	26.6	188	0	0
10	20.7	15.0	32.3	21.0	15.5	33.4	195.5	4.0	8.16
30	21.5	19.5	42.8	21.8	20.0	44.0	197.4	5.0	10.3
60	21.7	20.5	45.2	22.0	21.0	46.4	197.6	5.1	10.5
120	21.8	20.9	46.2	22.1	21.7	48.1	198.5	5.6	14.3
180	21.8	21.0	46.4	22.1	21.7	48.1	198.5	5.6	14.3

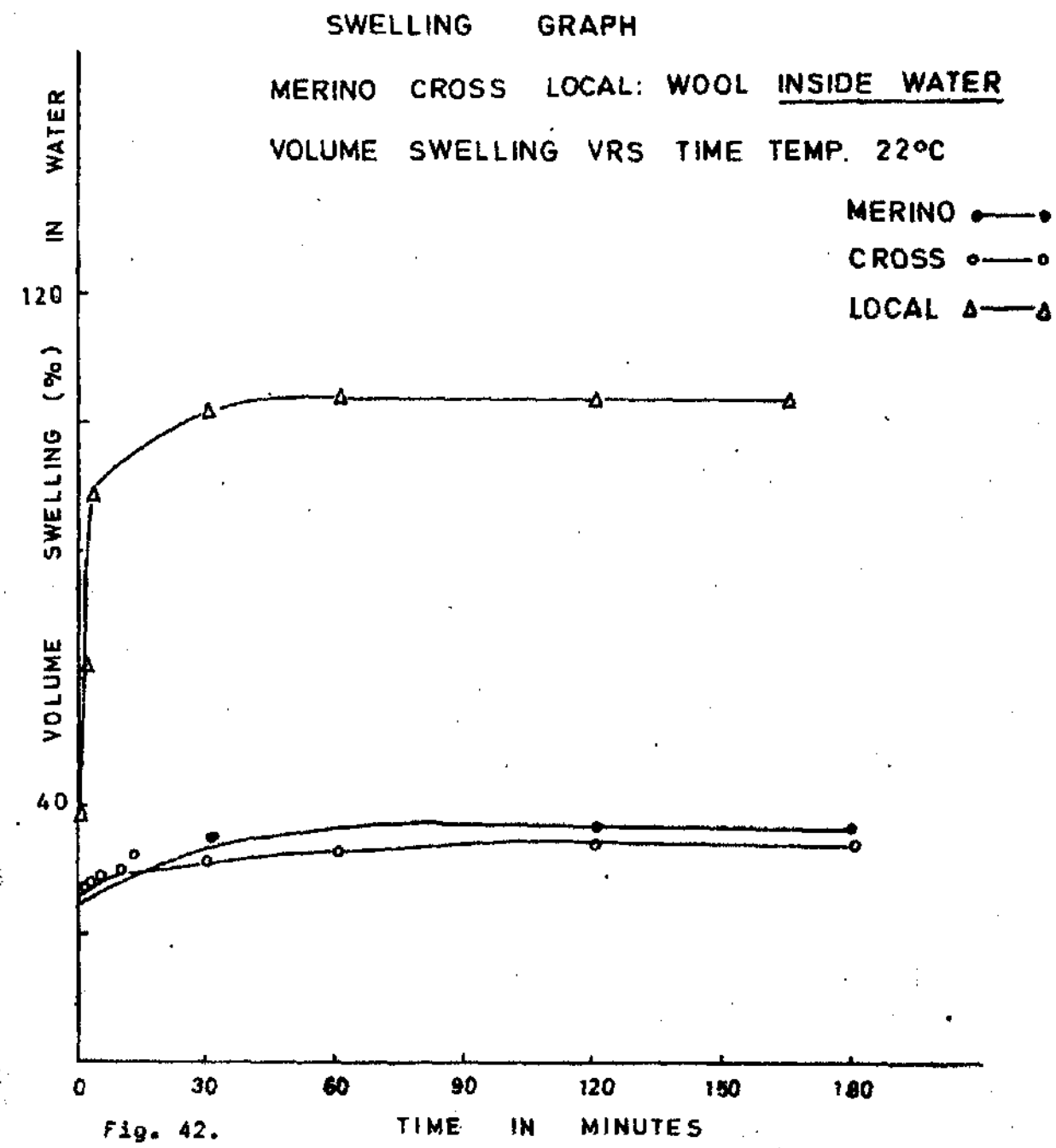

SWELLING GRAPH
MERINO CROSS LOCAL: WOOL INSIDE WATER
VOLUME SWELLING VRS TIME TEMP. 22°C
MERINO
CROSS
LOCAL
SWELLING (%) IN WATER
VOLUME
120
40
0
30
60
90
120
150
180
TIME IN MINUTES

Fig. 42.

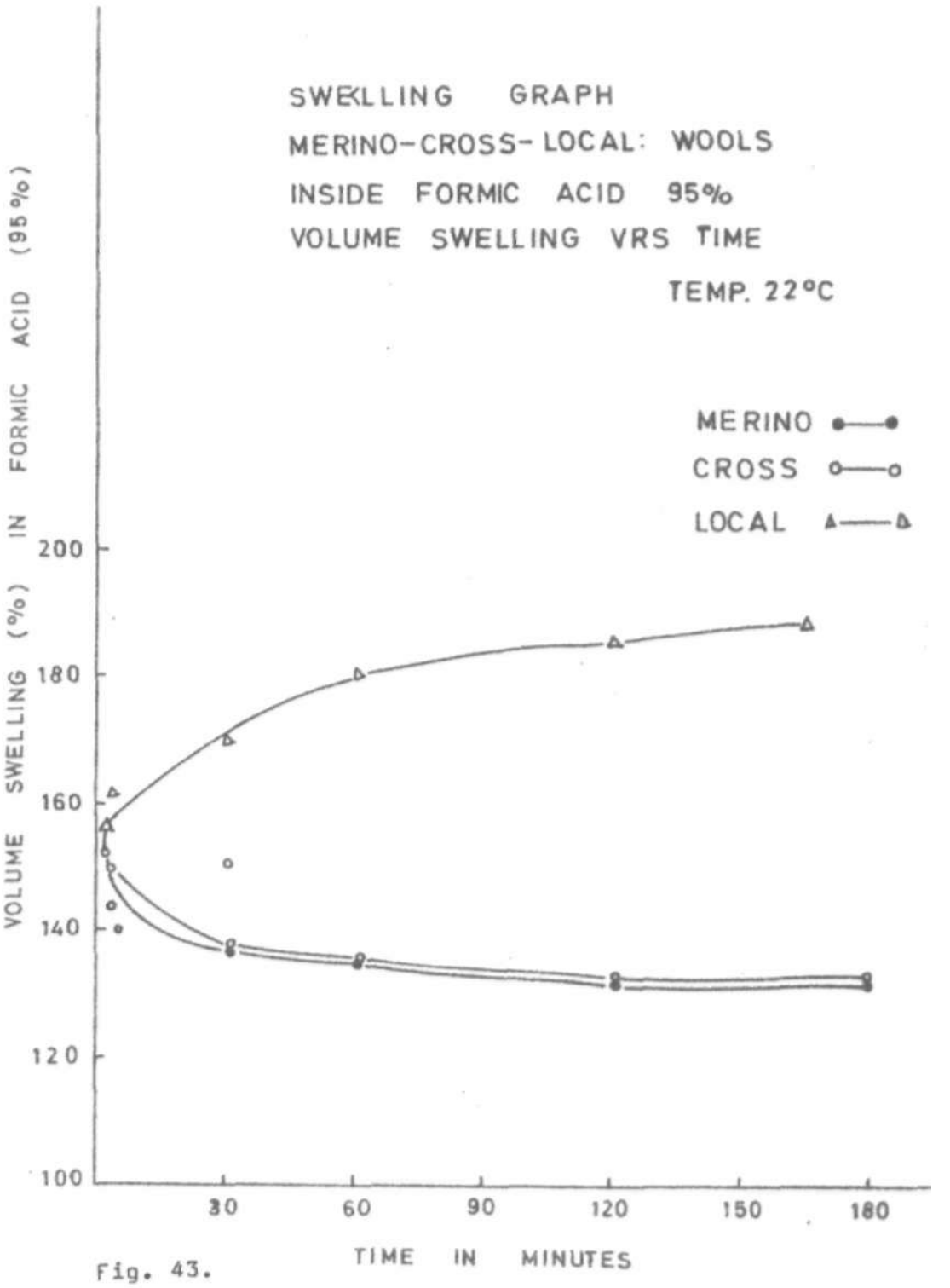

SWELLING GRAPH
MERINO-CROSS-LOCAL: WOOLS
INSIDE FORMIC ACID 95%
VOLUME SWELLING VRS TIME
TEMP. 22°C
MERINO
CROSS
LOCAL
VOLUME SWELLING (%) IN FORMIC ACID (95%)
200
180
160
140
120
100
30
60
90
120
150
180
TIME IN MINUTES

Fig. 43.

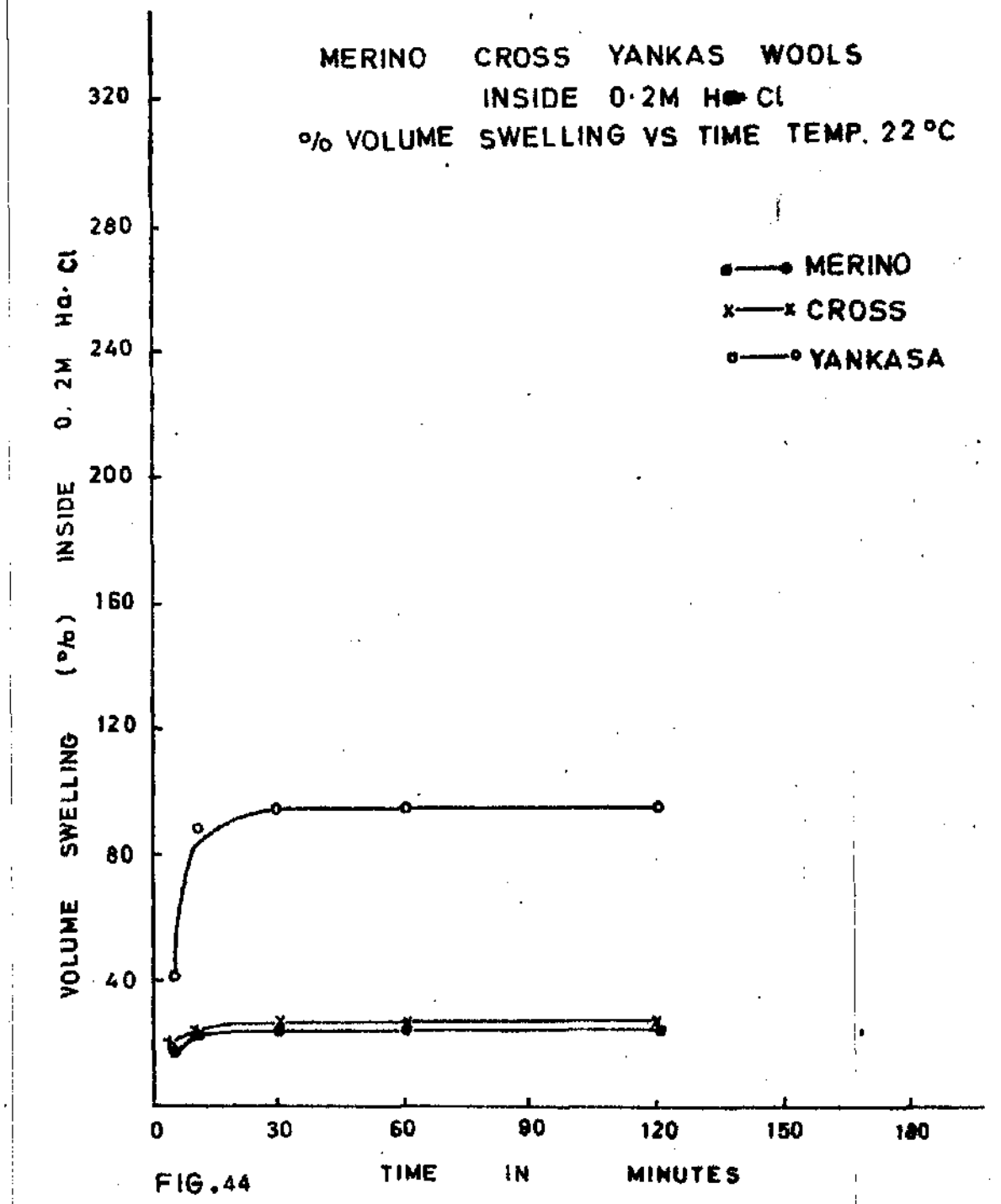

MERINO CROSS YANKAS WOOLS
INSIDE 0·2M HCl
% VOLUME SWELLING VS TIME TEMP. 22 °C
MERINO
CROSS
YANKASA
VOLUME SWELLING (%) INSIDE 0.2M Ha·Cl
320
280
240
200
160
120
80
40
0
30
60
90
120
150
180
TIME IN MINUTES

FIG.44

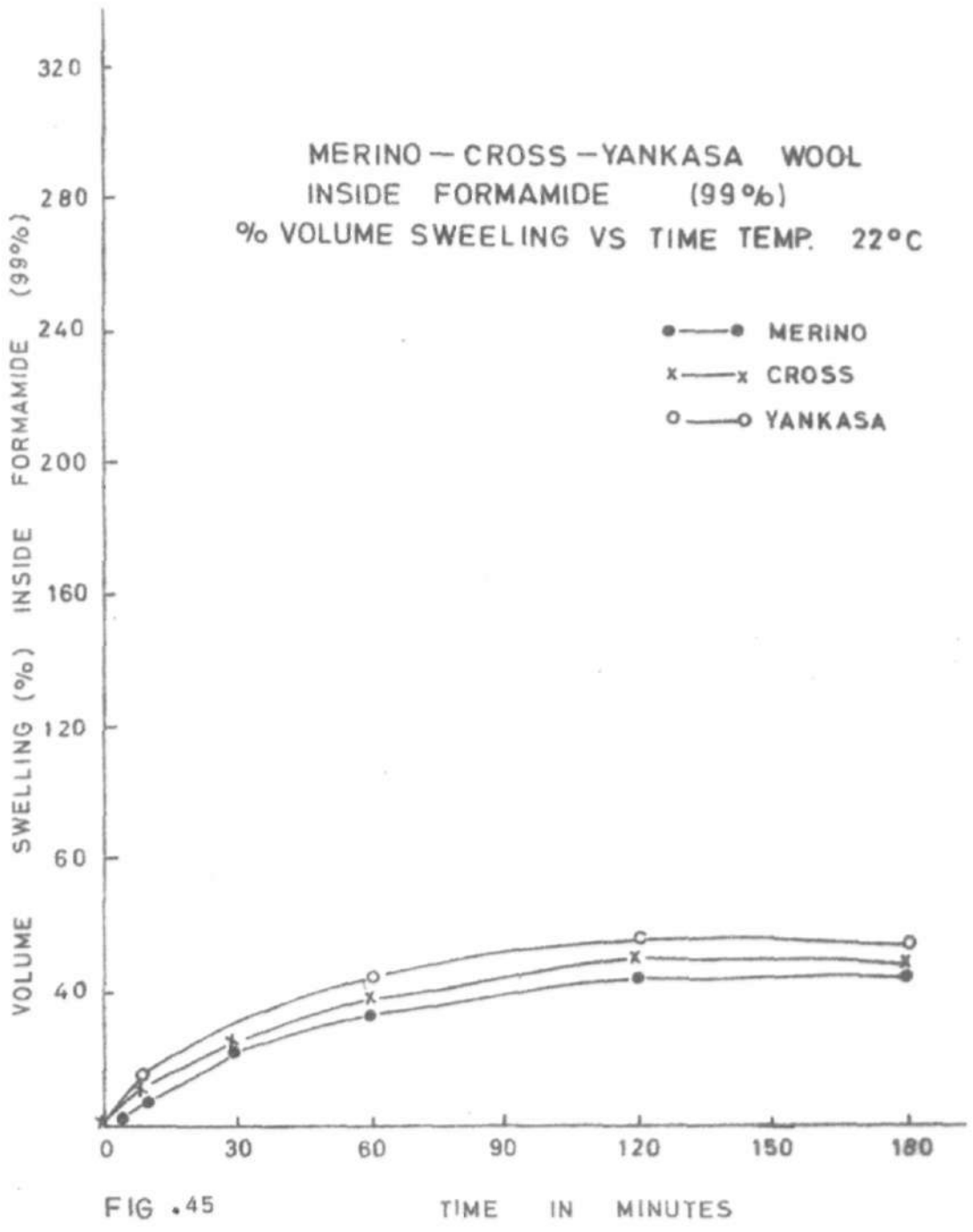

MERINO — CROSS — YANKASA WOOL
INSIDE FORMAMIDE (99%)
% VOLUME SWEELING VS TIME TEMP. 22°C
MERINO
CROSS
YANKASA
SWELLING (%) INSIDE FORMAMIDE (99%) VOLUME
320
280
240
200
160
120
60
40
0
30
60
90
120
150
180
TIME IN MINUTES

FIG .45

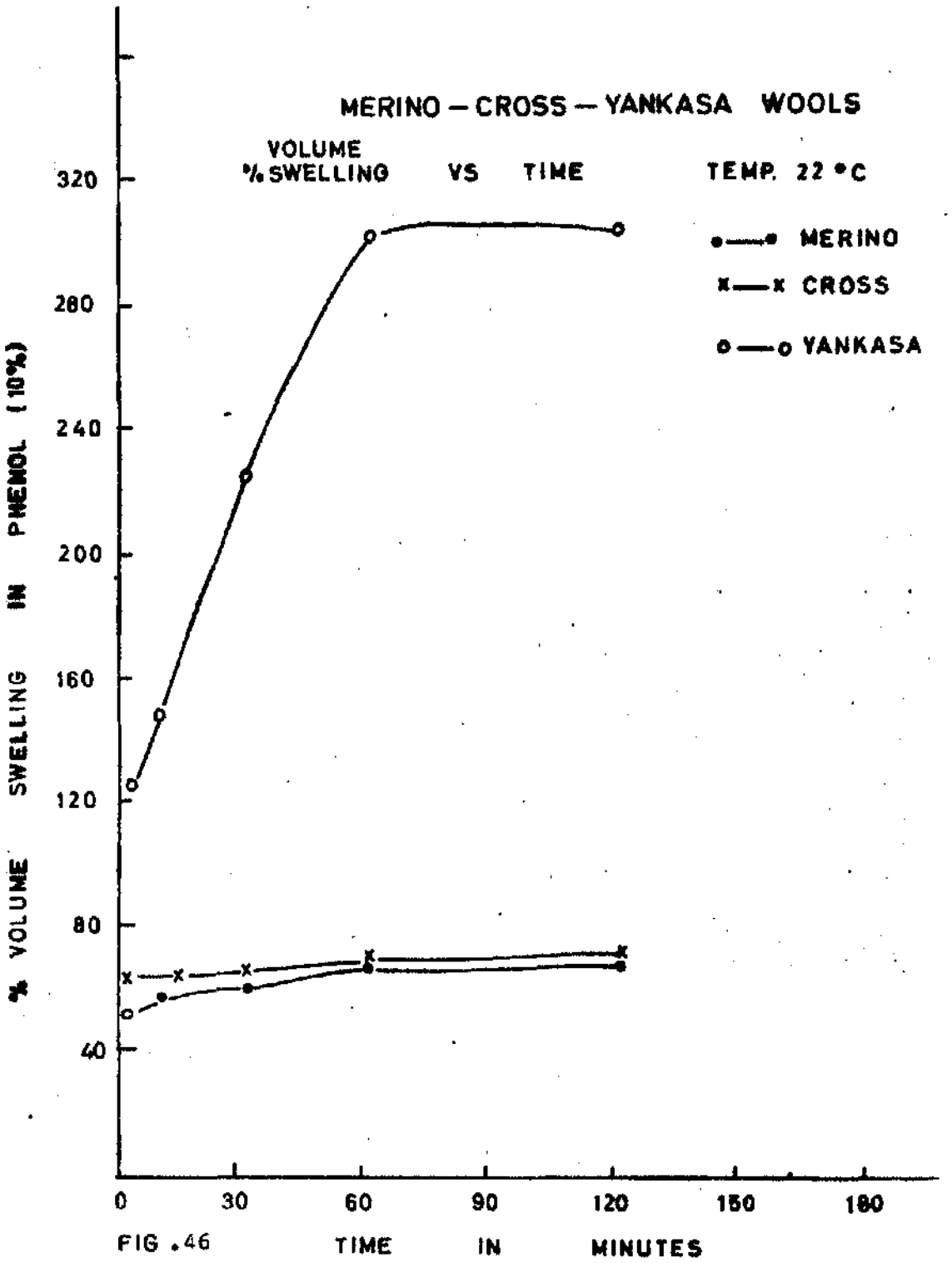

MERINO — CROSS — YANKASA WOOLS
VOLUME % SWELLING VS TIME
TEMP. 22 °C
MERINO
CROSS
YANKASA
SWELLING IN PHENOL (10%)
% VOLUME
320
280
240
200
160
120
80
40
0
30
60
90
120
150
180
TIME IN MINUTES

FIG .46

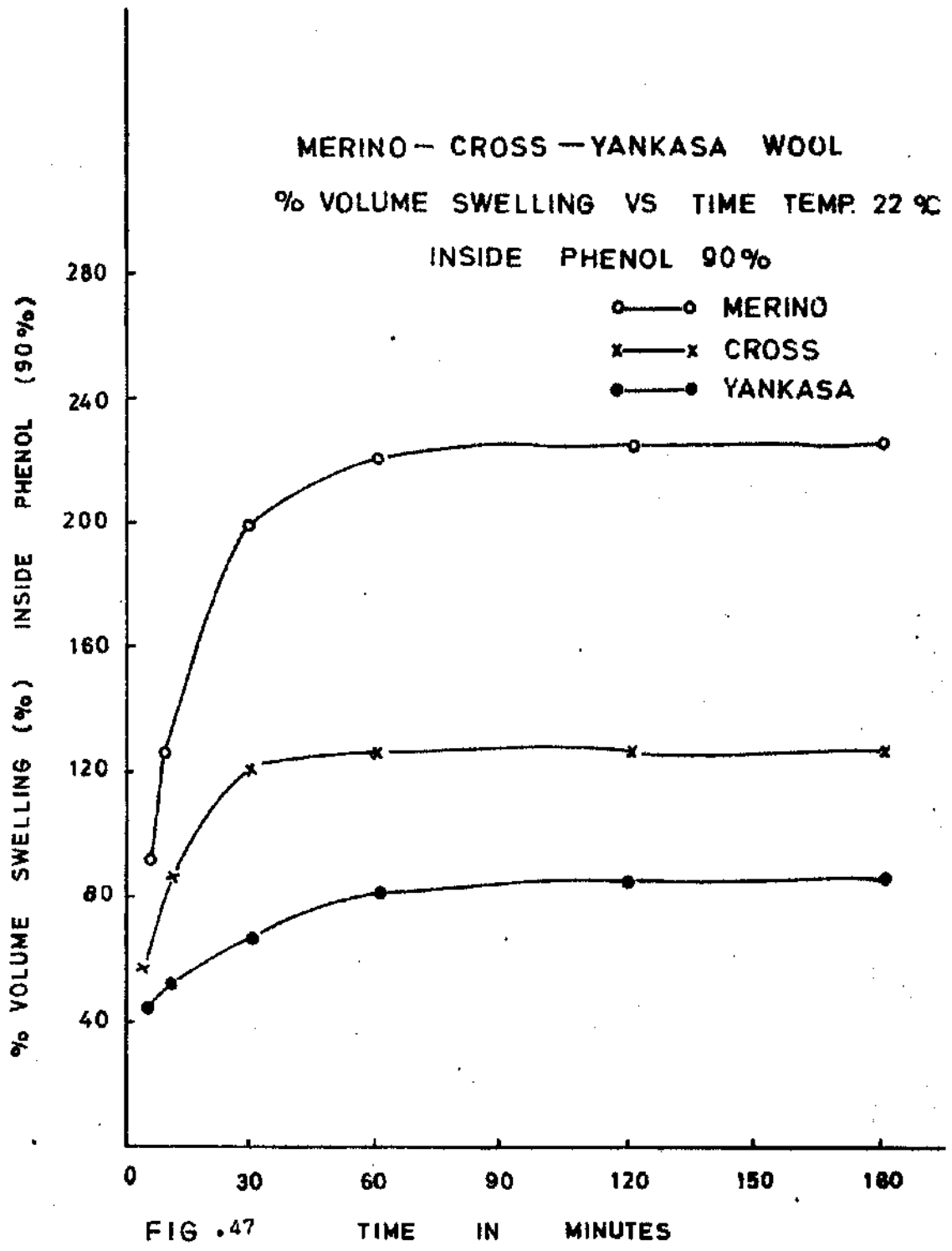

MERINO – CROSS – YANKASA WOOL
% VOLUME SWELLING VS TIME TEMP. 22 °C
INSIDE PHENOL 90%
MERINO
CROSS
YANKASA
% VOLUME SWELLING (%) INSIDE PHENOL (90%)
280
240
200
160
120
80
40
0
30
60
90
120
150
180
TIME IN MINUTES

FIG .47

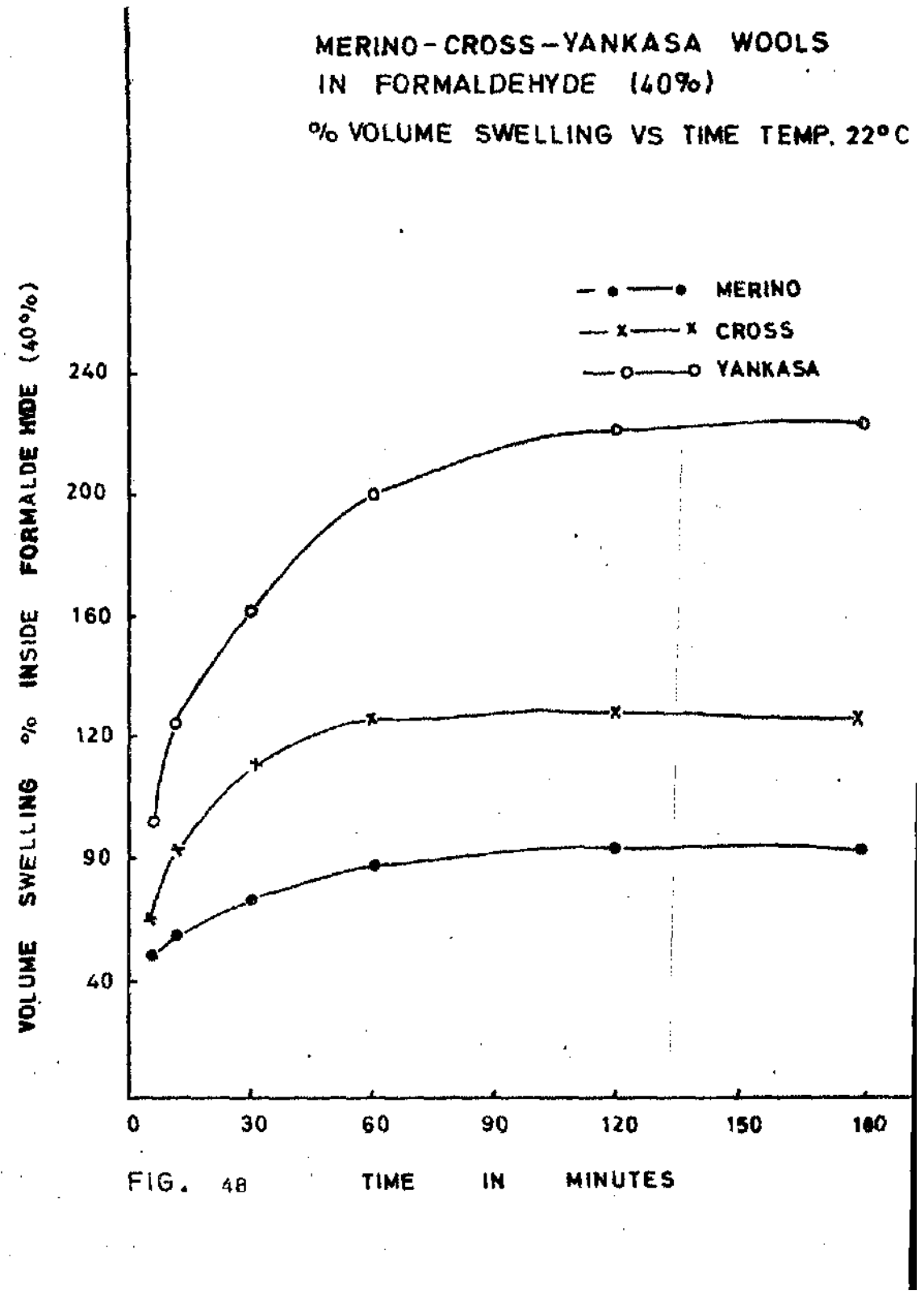

MERINO - CROSS - YANKASA WOOLS
IN FORMALDEHYDE (40%)
% VOLUME SWELLING VS TIME TEMP. 22°C
MERINO
CROSS
YANKASA
% VOLUME SWELLING INSIDE FORMALDE HYDE (40%)
240
200
160
120
90
40
0
30
60
90
120
150
180
TIME IN MINUTES

FIG. 48

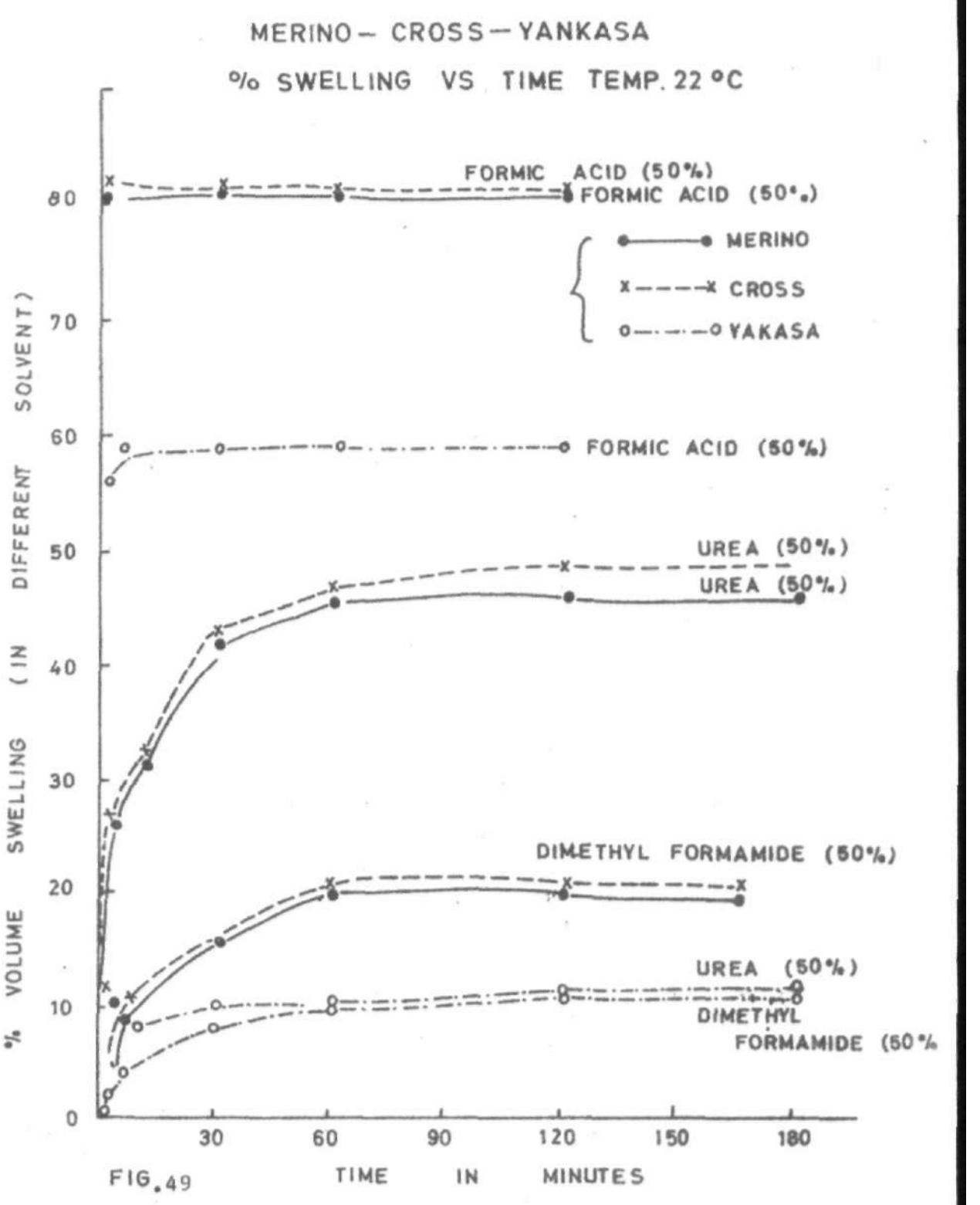

MERINO – CROSS – YANKASA
% SWELLING VS TIME TEMP. 22 °C
% VOLUME SWELLING (IN DIFFERENT SOLVENT)
TIME IN MINUTES
0
10
20
30
40
50
60
70
80
30
60
90
120
150
180
FORMIC ACID (50%)
FORMIC ACID (50%)
MERINO
CROSS
YAKASA
FORMIC ACID (50%)
UREA (50%)
UREA (50%)
DIMETHYL FORMAMIDE (50%)
UREA (50%)
DIMETHYL FORMAMIDE (50%

FIG. 49

Table No.47 SWELLING DATA

Hydrazine [98%] Temperature = 22°C

Time in Minute	Merino: diam. = 18.0 μ			Cross: diam. = 18.2 μ			Yankasa: diam. = 188μ		
	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume	Swollen diam.	% increase of diam.	% increase of volume
1	27.0	50	12.5	38.4	111	34.5	330.9	76.0	20.9
5	30.8	71	19.2	42.2	132	43.8	336.5	79.0	22.0
10	36.0	100	30.0	45.5	150	52.5	336.5	79.0	22.0
30	45.0	150	52.5	50.1	175	65.6	338.4	80.0	22.4
60	45.0	150	52.5	50.1	175	65.6	338.4	80.0	22.4
				(GLYCEROL)	100%				
30	18.0	0	0	18.2	-	-	188	-	-
60	18.0	0	0	18.2	-	-	189.9	1.0	2.0
120	18.0	0	0	18.3	0.5	1.0	191.5	1.9	3.8
180	18.0	0	0	18.3	0.5	1.0	192.3	2.3	4.7

APPENDIX 5

HYSTERESIS CURVES DUE TO EXTENTION 29



Merino in formic acid (50%)

10 mins.

Scale: 10g



Merino in formic acid (50%)

5 mins.

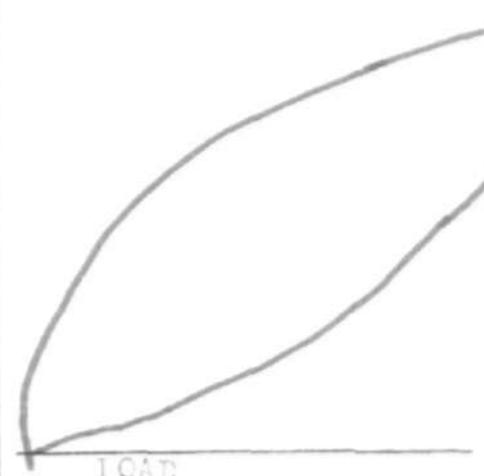
Scale: 10g



Merino in phenol

120 mins.

Scale: 10g



Merino in phenol

30 mins.

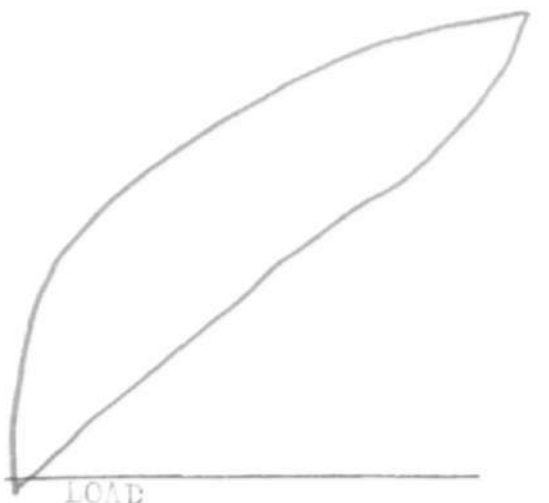
Scale: 10g



LOAD

Cross in formic acid
10 mins.

Scale : 10g



LOAD

Cross in formic acid
5 mins.

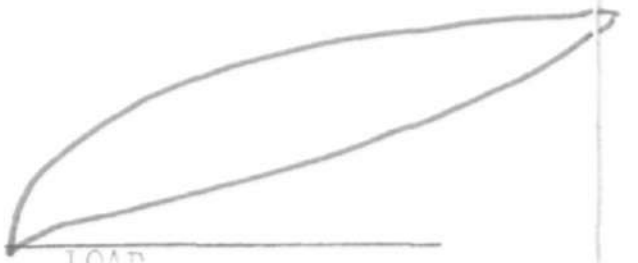
Scale: 10g



LOAD

Merino in phenol
120 mins.

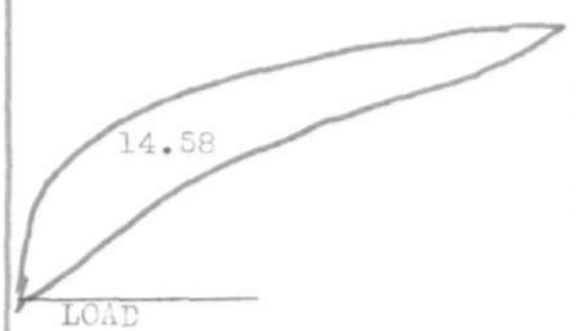
Scale: 10g



LOAD

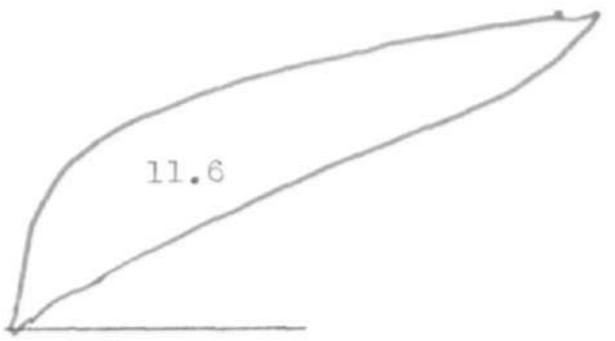
Merino in phenol
60 mins.

Scale:10g



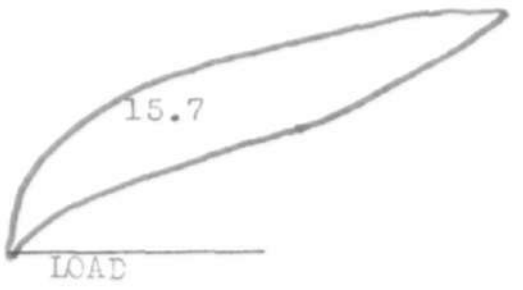
Merino in absolute alcohol

10 mins. Scale:20g



Merino in absolute alcohol

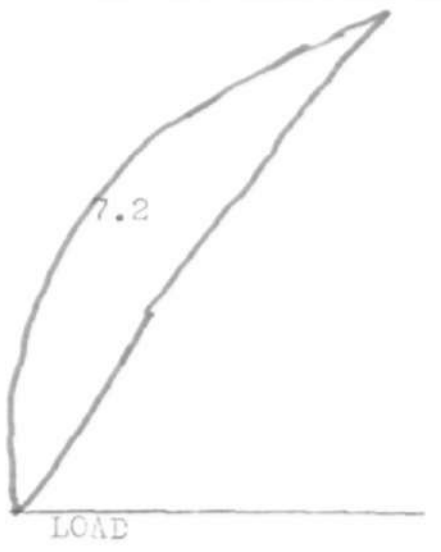
5 mins. Scale:20.g



Cross in 0.2 N HCl

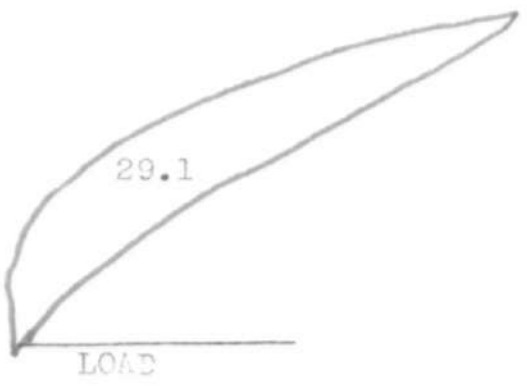
10 mins.

Scale: 10g



Cross in Thioglycollic acid

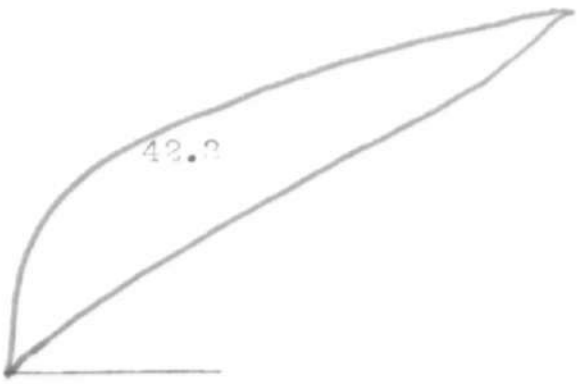
10 mins. Scale:10g



Merino in absolute alcohol

10 mins.

Scale: 20g



Merino in absolute alcohol

5.mins.

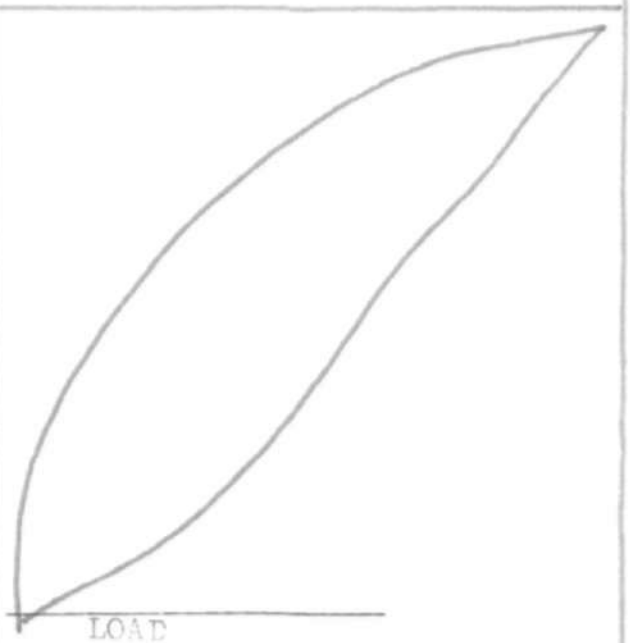
Scale : 20g



Merino temp. 90°C

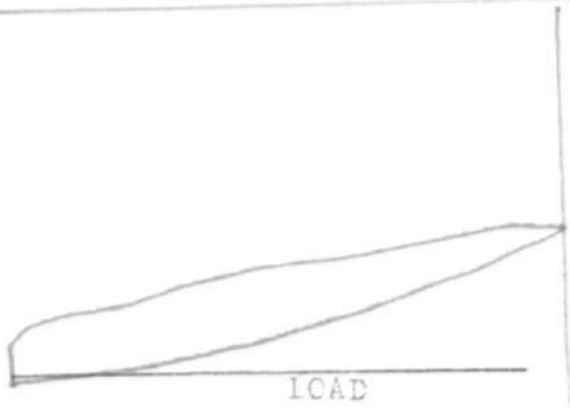
r.h. 100%

Scale : 10g



Merino in ice ,Temp. 0°C

r.h. 100 %, Scale: 10g



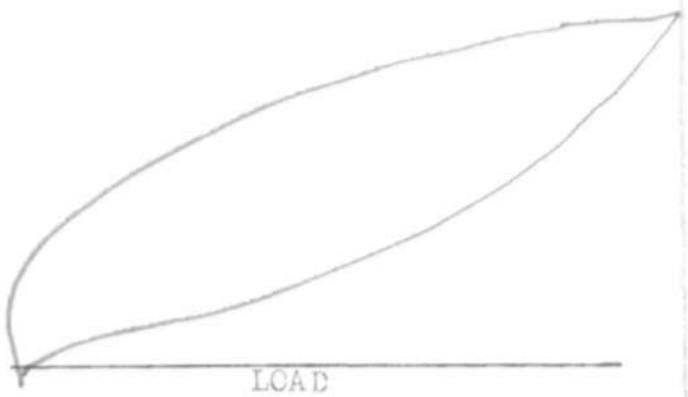
Merino Dry
Temp. 22°C
r.h. 0%
Scale: 20g



Merino Temp. 0°C
r.h. 100 %
Scale: 20g



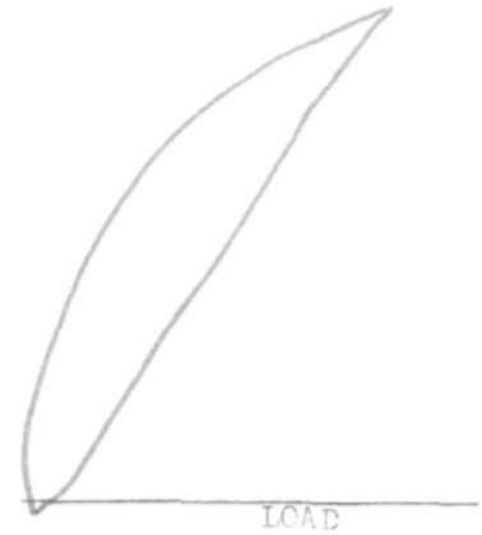
Merino Temp. 90°C
r.h. 100%
Scale: 10g



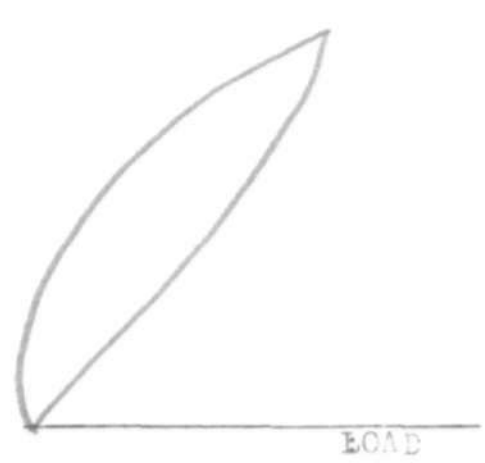
Merino Dry
Temp. 22°C
r.h. 0% Scale: 20g



Cross in absolute alcohol
10 mins.
Scale: 10g



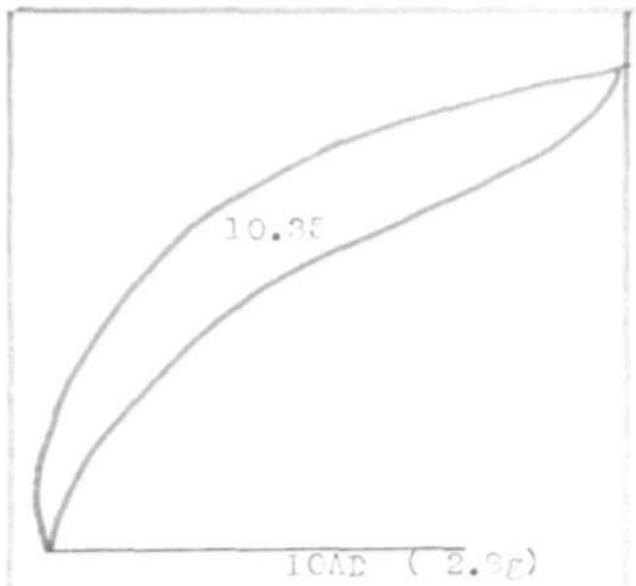
Cross in thioglycollic acid
10 mins.
Scale: 10g



Merino in formic acid
10 mins.
Scale. 20g



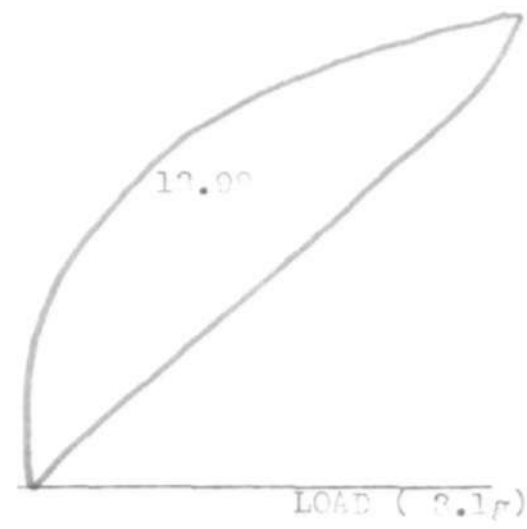
Merino in formic acid
5 mins.
Scale: 20g



Cross in formic acid

10 mins.

Scale; 10g



Cross in formic acid

5. mins.

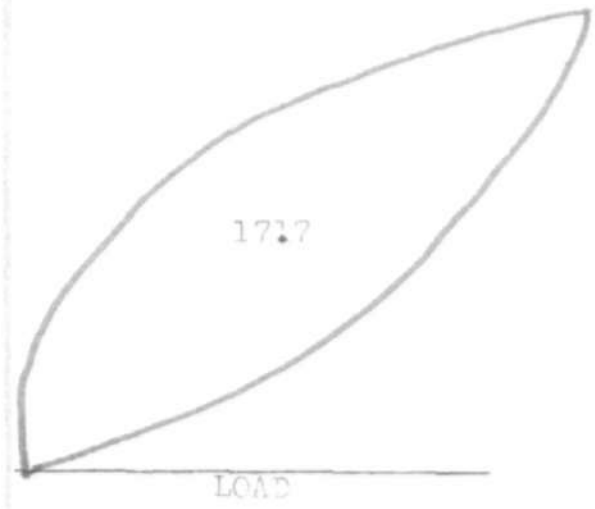
Scale; 10g



Merino in water

Temp. 90°C

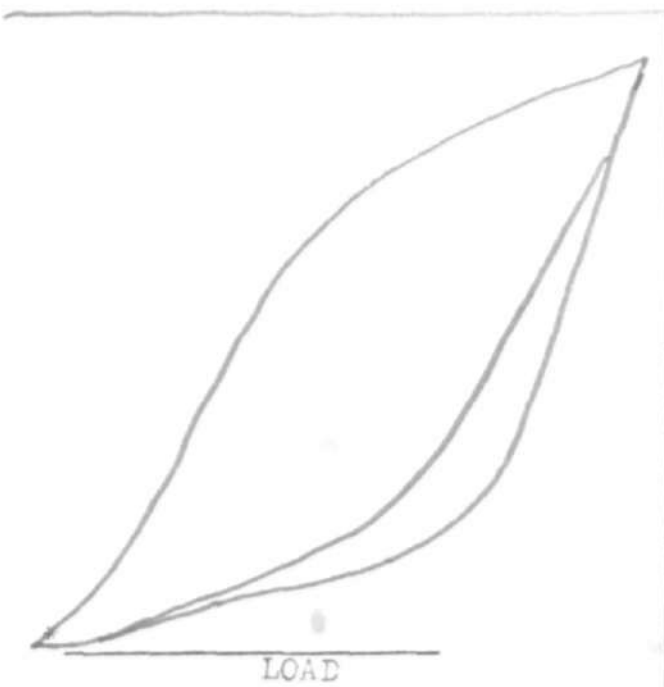
Scale;20g r.h. 100%



Merino in phenol

20 mins.

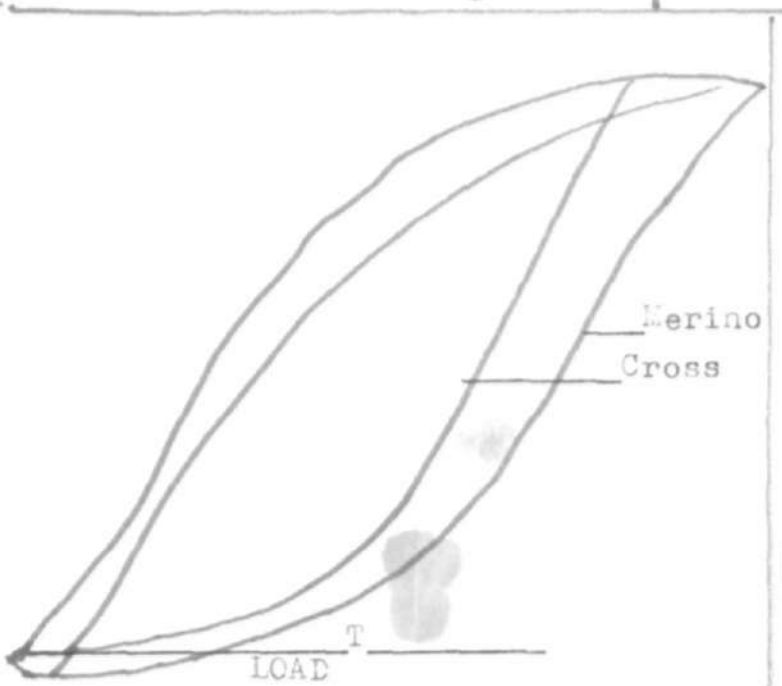
Scale: 20g



Cross in $NiCl_2$ (o.33M)
72 hours. Scale: 10g



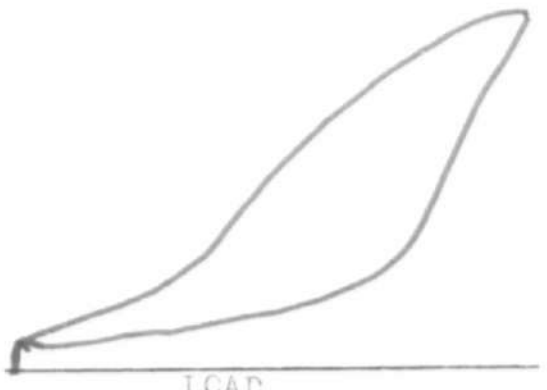
MERINO in 0.33 M $CoCl_2$
72 hours Scale: 10g



MERINO and CROSS
in 0.33M $NiCl_2$
72 hours Scale: 10g



CROSS in 0.33M $CoCl_2$
72 hours
Scale: 10g



Yankasa in 0,33M $ZnCl_2$

72 hours

Scale: 50g

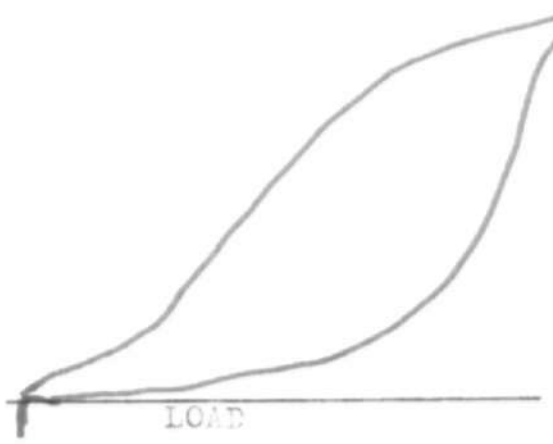


Merino in formic acid

10 mins.

Temp. 22^{o}C

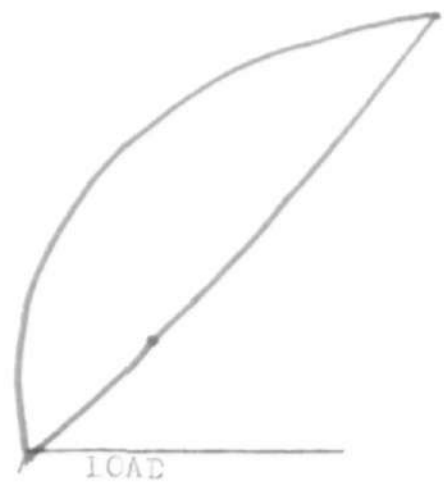
Scale: 20g



Yankasa in water

Temp. 22^{o} C

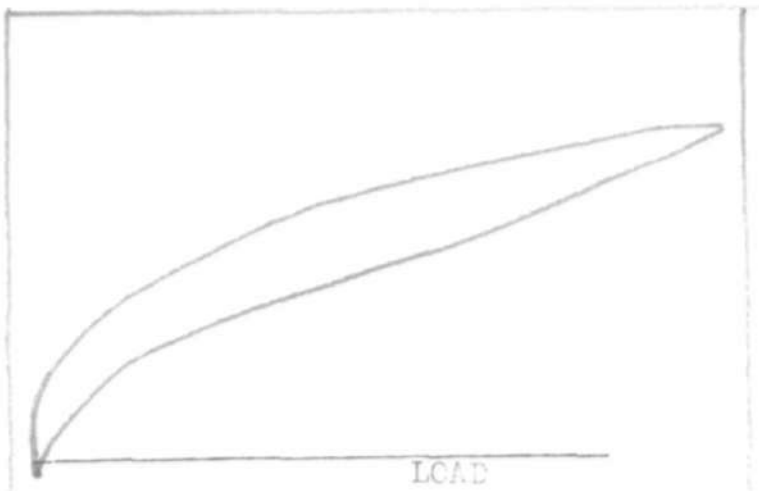
Scale: 50g



Merino in formic acid

5 mins.

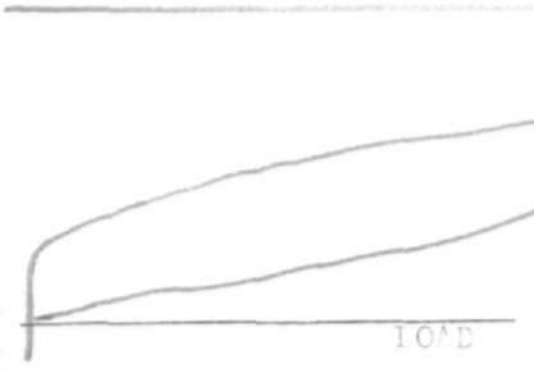
Scale: 20g



Cross dry
Temp. 22°C
r.h. 0%
Scale: 20g

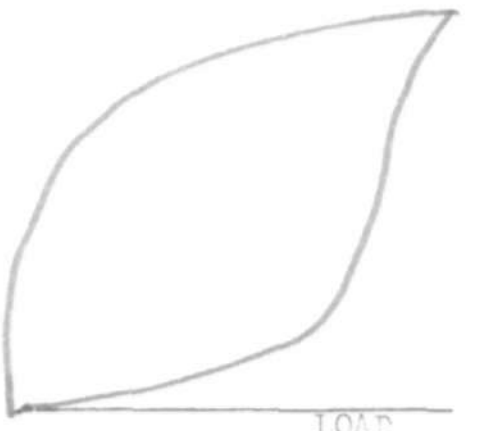


Cross in side water
72 hours
Temp. 22°C
Scale: 20g

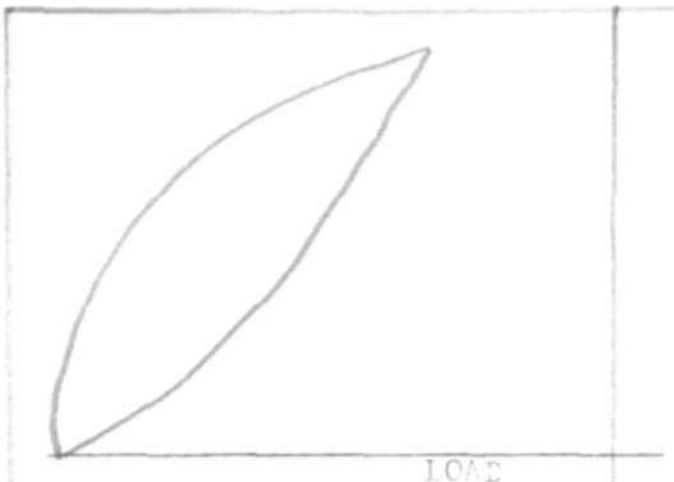


Merino in formamide

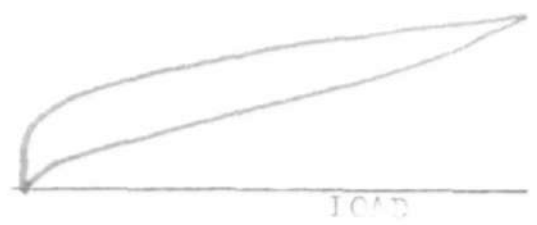
10 mins.
Scale: 20g



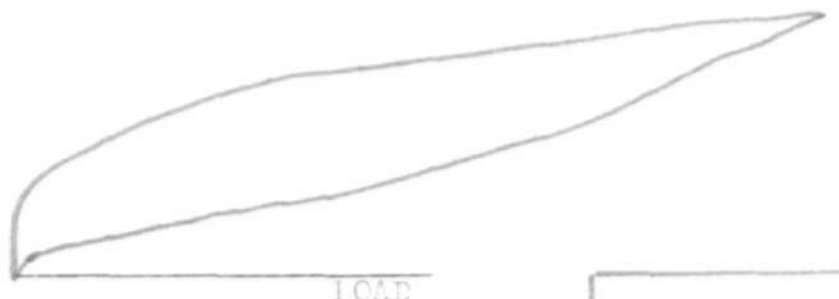
Merino in formamide
5 mins.
Scale :20g



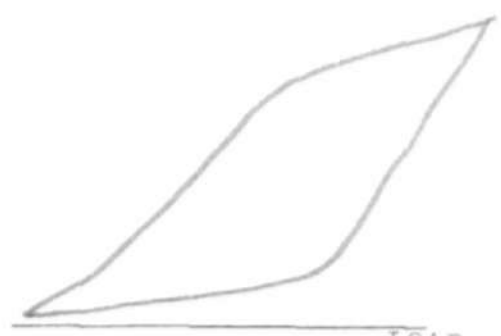
Merino inside water (ice)
Temp. 0°C
r.h. 100%
Scale: 10g



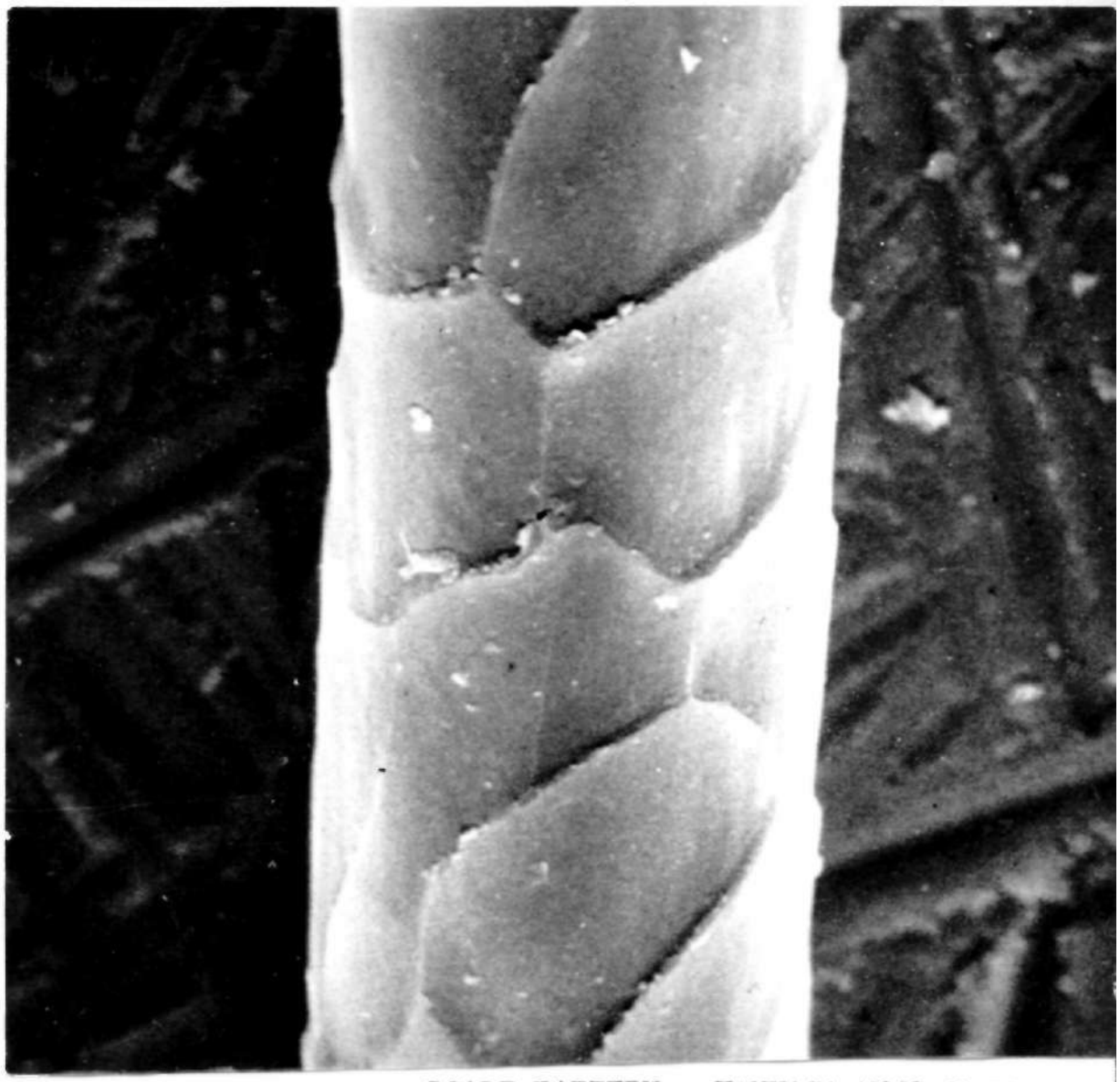
Merino dry
r.h. 0%
Temp. 22°c
Scale: 20g



Cross in formamide
10 mins.
Scale: 10 g



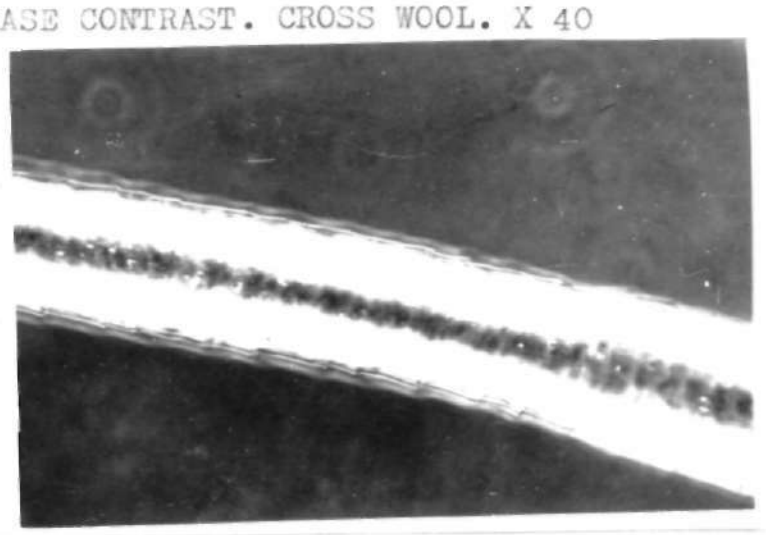
Yankasa wool in 0.33M $CoCl_2$
72 hours Scale: 50g



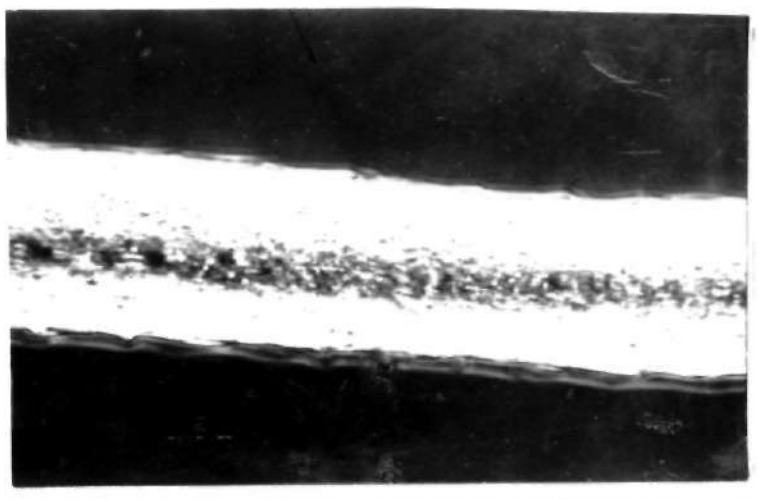
SCALE PATTERN - YANKASA WOOL X 200



SURFACE.PHASE CONTRAST. CROSS WOOL. X 40



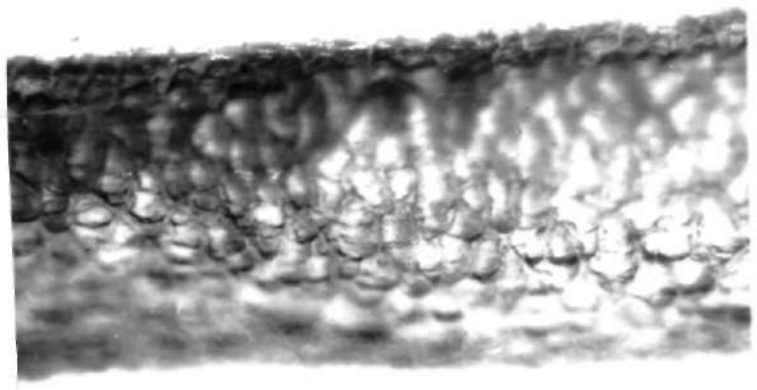
SURFACE. PHASE CONTRAST. MERINO WOOL X90



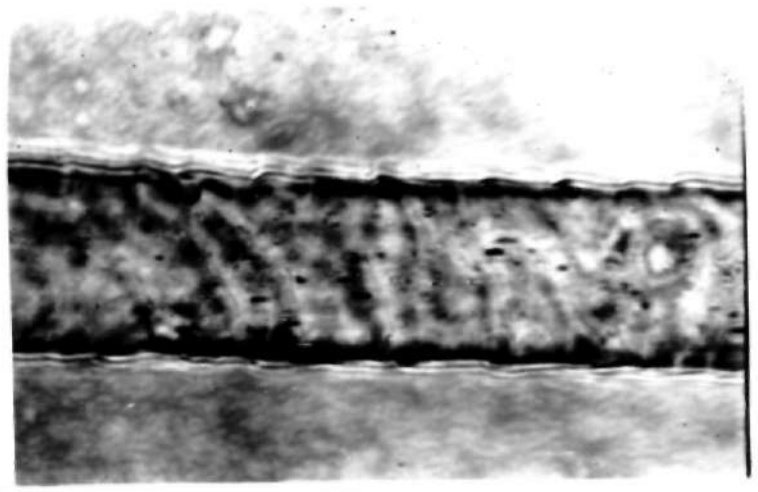
SURFACE. PHASE CONTRAST. BALUCHI WOOL. X40



SURFACE: YANKASA WOOL. X10



SURFACE: YANKASA WOOL. X25



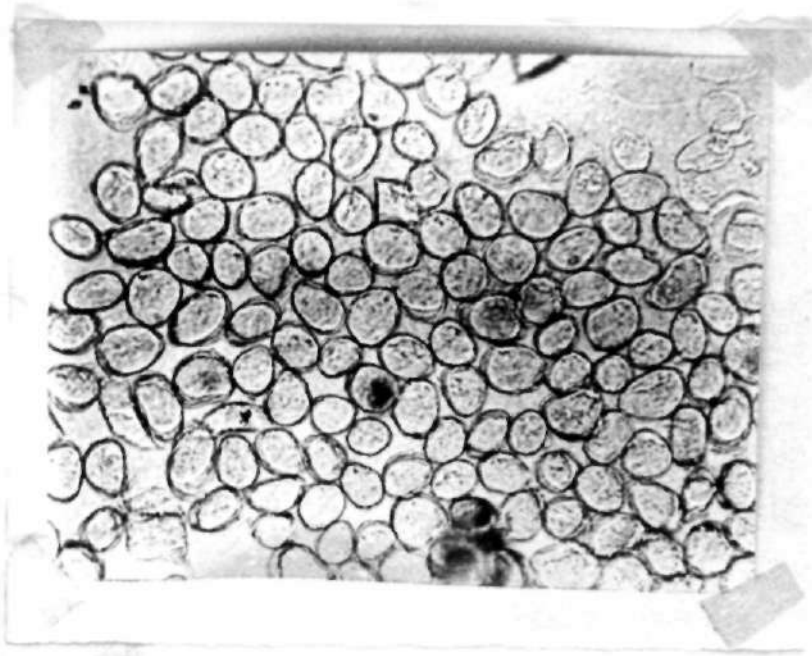
SURFACE: CROSS WOOL. X90

SURFACE BALUCHI X90



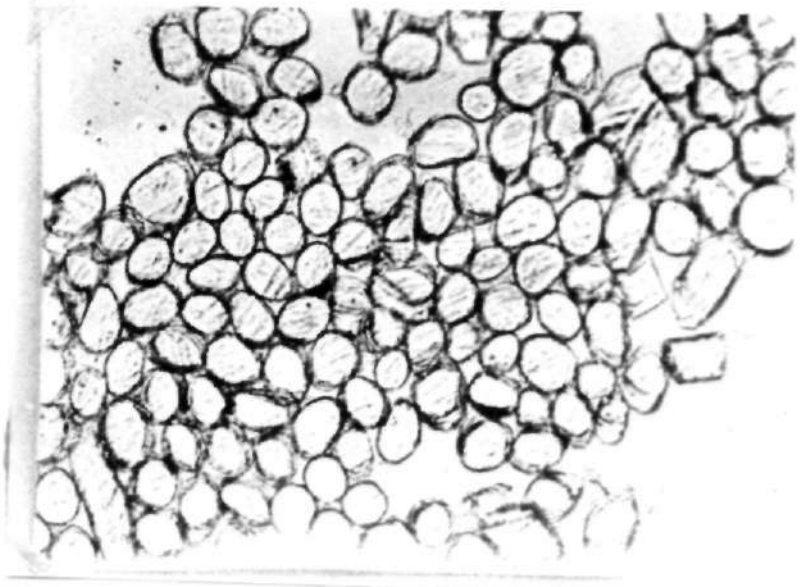
SURFACE CROSS WCCL X90





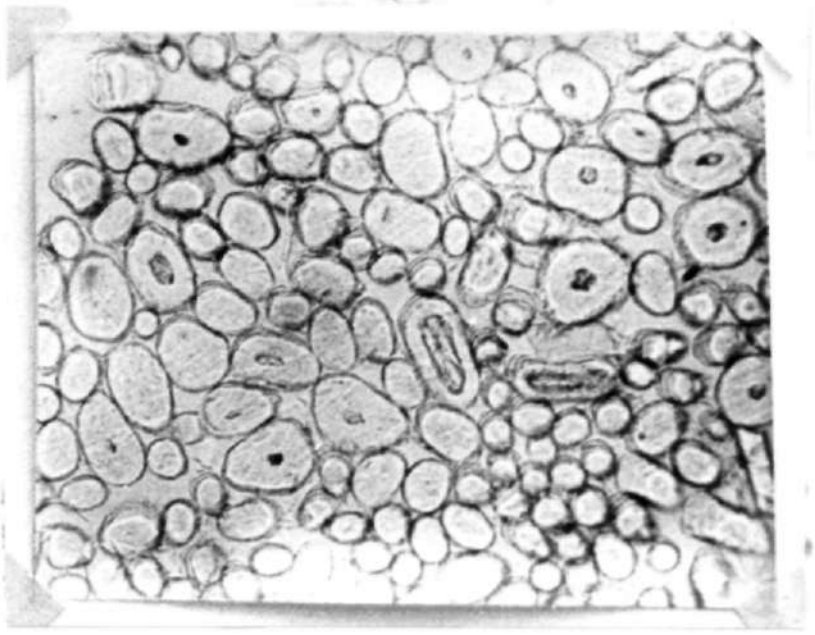
CROSS-SECTION MERINO WOOL

X120



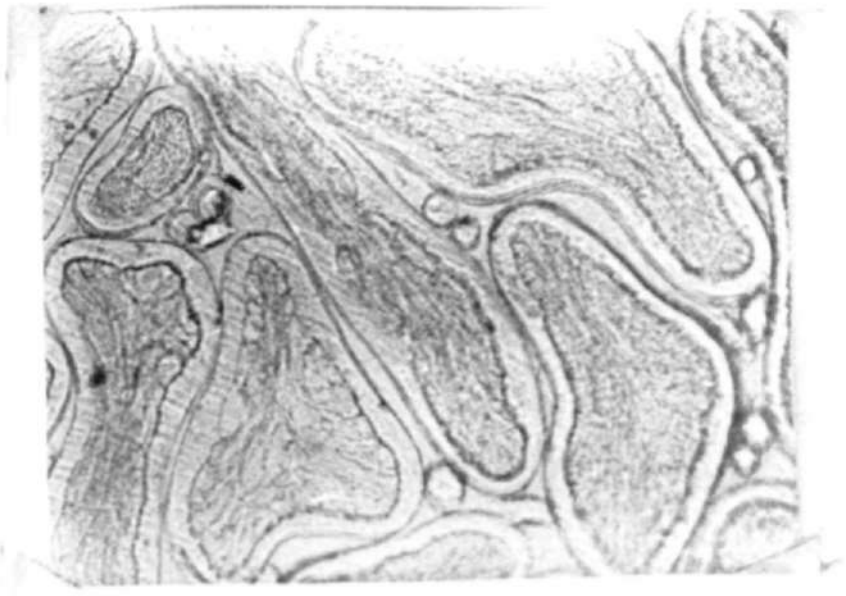
CROSS-SECTION MER CROSS WOOL

X120



CROSS-SECTION. BALUCHI WOOL .

X120



CROSS-SECTION. YANKASA WOOL.

X120