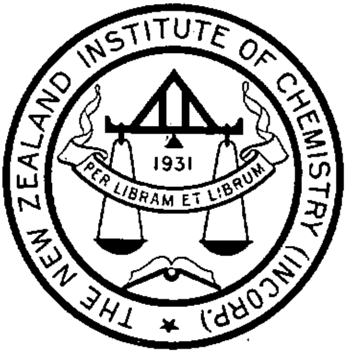
Vol. XI—No. 3 September, 1947

JOURNAL

of the

NEW ZEALAND
INSTITUTE of CHEMISTRY



Published by the New Zealand Institute of Chemistry (Inc.)
Wellington, New Zealand

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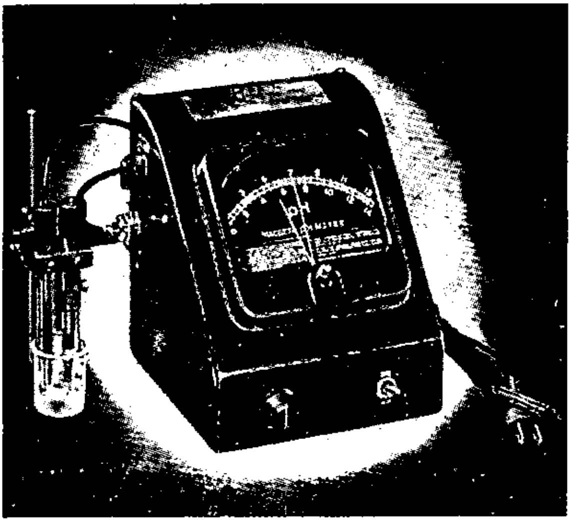



SHELL

JOURNAL
of the
NEW ZEALAND INSTITUTE OF CHEMISTRY

VOLUME XI. SEPTEMBER, 1947 NO. 3

PRESIDENTIAL ADDRESS, 1947.

THE CHEMISTRY OF WOOL.

(F. G. Soper, Ph.D., D.Sc., F.R.I.C. F.N.Z.I.C)

It is my privilege this evening to deliver the annual Presidential Address to the N.Z. Institute of Chemistry, a privilege which is at the same time a responsibility of which I am deeply conscious. In selecting as my subject the Chemistry of Wool I have been influenced by the fact that we have had the pleasure in recent years of listening to expert surveys of chemical endeavour and achievement over a wide field and it may not be inappropriate therefore this year to consider advances in knowledge of a particular subject, and one which concerns a nationally important commodity.

It is significant of the new relation which is emerging overseas between the universities and industry that much of the earlier fundamental scientific work on this industrially important commodity was carried out in the Universities. This association of universities with industry in Great Britain began in the middle of last century, but it is only comparatively recently that the scientists and industrialists have discovered mutual interests and a common language. There is in the first instance, the enforced interest that the university trained scientist is needed increasingly in industry, and it is the function of the university, whilst preserving all that is essential to a training on the fundamental aspects of science, so to adjust curricula to provide men able to fill the diverse needs of industry. Moreover particularly in Great Britain and in the United States, professors and lecturers in the science departments tend to be consulted by industry and so acquire a knowledge of industrial problems. There are those who tend to decry such association but in my considered opinion, chemistry in the university has never suffered from its association with industry, but on the contrary it has gained by having its field of interests extended. This in turn has resulted in a freshness of work in fundamental chemistry.

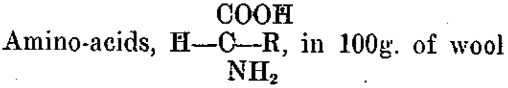
There has been no lack of freshness in fundamental work in chemistry in the period between the two wars. It has been a remarkably fruitful period, and not least in the field of natural products. New methods of separation of those complex mixtures, produced in the animal and vegetable kingdoms, have been devised and have initiated the now familiar cycle of isolation of the pure substance, determination of its constitution, its synthesis and the syntheses of chemically related substances. Here are fascinating chapters.

Whilst specialisation is increasingly necessary, yet it seems even more necessary for some re-synthesis of the divisions of sciences in the training of the chemical worker. It is, for example, much more necessary than formerly for the specialist in organic chemistry to know a good deal about physical chemistry and its techniques. This is also true as between the separate sciences. If the scientist is being recognised as useful in industry today, it is because he has not over-specialised. He must know something of a wide field. Indeed, the time has come, even if it is not overdue, for the university course for the B.Sc. degree, to extend over a period of 4 years, instead of the present 3 years. In this extended course when it comes, there should be some provision not only for a broader basis of scientific study, but also for some training in lucidity of expression. Lucidity of thought and of expression is needed as never before, if the humanities and science are to become mutually appreciative of each other, and never before has this mutual appreciation been more desirable.

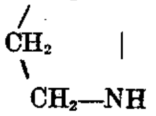
The advance in our knowledge of wool structure illustrates well the need for investigation on a wide front. Our increased knowledge of its atomic architecture is due to the close collaboration of workers in physics and chemistry, particularly, in the first instance in the University of Leeds. Chemically wool belongs to that class of substances known as keratins, and is of similar composition to horn and feathers. By acid hydrolysis it is possible to obtain a mixture of amino acids from wool, from which it has been possible to separate and identify eighteen distinct amino acids.

The amino acids which have been thus isolated from wool are shown in Table I and the amounts obtained by various recent workers have been critically assessed by Astbury (1) in 1942.

TABLE I.



Amino-acids, $H-\overset{COOH}{\underset{NH_2}{C}}-R$, in 100g. of wool

Acid	**R**	**M**	**Yield**	**Gm. residues**
glycine	$-H$	75	6.5	0.0870
alanine	$-CH_3$	89	4.13	0.0464
serine	$-CH_2(OH)$	105	10.3	0.0981
valine	$-CH(CH_3)_2$	117	4.8	0.0410
leucine etc.	$-CH_2CH(CH_3)_2$	131	11.3	0.0863
phenyl alanine	$-CH_2C_6H_5$	165	3.75	0.0227
tyrosine	$-CH_2C_6H_4(OH)$	181	4.65	0.0257
tryptophan	$-CH_2C_8NH_6$	204	1.8	0.0088
threonine	$-CH(OH)CH_3$	119	6.4	0.0538
lysine	$-(CH_2)_4NH_2$	146	2.65	0.0182
arginine	$-(CH_2)_3(NH)_2CNH_2$	174	10.3	0.0592
histidine	$-CH_2C_3N_2H_3$	155	0.7	0.0045
aspartic acid	$-CH_2COOH$	133	6.57	0.0494
glutamic acid	$-(CH_2)_2COOH$	147	14.1	0.0959
cystine/2	$-CH_2-S-$	120	11.9	0.0989
methionine	$-(CH_2)_2SCH_3$	149	0.7	0.0047
proline		115	6.8	0.0591
			TOTAL	0.8597
amide nitrogen		14	1.13	0.081

The composition in terms of amino acid content is not constant, for the wool fibre is not a homogeneous structure. By treatment with concentrated ammonia at room temperature or by the action of buffered solutions of trypsin, it may be separated into its cellular elements. Three distinct parts may be recognised, the scale or cuticle, the cortex made up of long shaped cells and occasionally a medulla.

The cuticle cells are flat oval-shaped bodies about 30 microns in diameter and about 1 micron thick, whilst the corticle cells are about 100 microns long. Work was carried out by Geiger (2) in 1944 on the composition of the scales, for by special treatment the scales may be left intact and subsequent analysis of this fraction reveals a higher cystine and lower arginine and tyrosine content. The higher cystine content of the scales was first recognised by Trotman and Sutton in 1926. The composition of the fibre itself varies along its length particularly as regards its cystine content which appears to depend on nutritional factors when the fibre was being formed.

Attempts to mould the results of amino acid analysis of this heterogeneous structure into a Bergmann-Niemann frequency distribution must therefore be accepted with caution. Since 1943 electron micrographs have been obtained which have further emphasized the heterogeneity of the structure. Last year Mercer and Rees (4) found that the cuticle cell fragments obtained by grinding or scraping show a relatively smooth surface whereas cells isolated by the action of trypsin possess a clearly defined surface structure which is pitted or honey-combed. These preserve their appearance even after prolonged retting in enzyme solutions. Mercer terms the digestible material as k_1 and the resistant component as k_2. When the whole fibre is treated with trypsin, the intercellular cement, holding the cuticle to the cortex and the cortical cells together, is also removed so that there is a close similarity of the k_1 of the cuticle with the intercellulalr cement. This intercellular cement was given the name "lanain" by Haller and Hall in 1936 who found cystine and cystein groups absent.

Electron micrographs of fragments of the cortical cells (5) obtained by grinding, show dense fibrils and a less dense interfibrillar component which is apparently digested by trypsin, whilst the fibrils are not. The inter-fibrillar component is reported as amorphous and solid but can be drawn into threads in a manner closely resembling the behaviour of a viscous rubber solution.

In the light of these facts, there appears little hope that chemical work based on isolation of molecular fragments may lead to complete knowledge of the structure of keratin. Nevertheless, very interesting work is now proceeding on the partial hydrolysis of wool and the identification of the dipeptides and tripeptides which result. This investigation has been developed by Synge and Martin (7) and may serve to check structures which have been advanced on other grounds. These workers at the Wool Industries Research Association, Torridon, have developed a technique described as partition chromatography. The basis of this method is the fact that if an aqueous solution of amino acids is extracted on a counter current principle with a solvent immiscible with water, the various amino acids tend to be carried forward by the solvent at different rates depending on their relative partition coefficients. This was developed by Gordon, Martin and Synge, in 1943, into the use of a silica column in which the water phase is held on the silica and the amino acids applied to the top of the column and some suitable non-aqueous solvent allowed to percolate down. In this way the acids gradually moved down the column. Later cellulose in the form of strips of filter paper was used as the substrate, on which absorbed water was held immobile whilst various solvents partially miscible with water were used to carry the amino acids down the paper.

Since no single solvent gives complete separation of the amino acids, the paper is sometimes treated first with a solvent such as collidine and then turned through a right angle and treated with another solvent such as water-saturated phenol producing a two dimensional chromatogram. The paper after drying is sprayed with ninhydrin which forms coloured complexes with the amino acid. The indentification of any particular amino acid is possible by running a duplicate chromatogram using a known acid, its position at a given time being characteristic of that acid. The position is determined by the rate of movement of non-aqueous solvent and the distribution coefficient of the substance between the two solvents.

In examining partial hydrolysates, the peptide is revealed by a colour reaction and the coloured paper strip is used as a guide to cutting a second paper strip run at the same time and the peptide is then washed off, hydrolysed and the free amino-acids again examined by the paper chromatogram method and identified. A large number of dipeptides and some tripeptides have been examined and identified in this way (8). The results indicate that wool is very complex, for example, glutamic acid may have attached to it in the dipeptide fragment, residues of any of the following: glutamic acid, aspartic acid, serine, tyrosine, glycine, alanine, leucine and possibly valine. There is as yet no indication of any regular sequence of amino-acids in the polypeptide chain.

What however has been recognised for some time from the chemical work is that since all eighteen amino acids isolated are alpha-amino acids the structure of the parent protein must be based on Fischer's theory of polypeptide links.

From a number of investigations it has been proven that all the amino-acids which have been isolated have the same relative stereochemical configuration. The hydrogen atom, amino-group, carboxyl group and the R group are arranged around the carbon atom in the same way for each acid. The result of this is that in the polypeptide the R group along the extended polypeptide chain stick out alternately up and down. If, as appears feasible, a polypeptide may be synthesized in vivo at a fat-water interface one may expect polar groups to be attached on one side, i.e., from the water phase, and non-polar groups from the non-aqueous phase. This would result in an alternation of polar and non-polar groups as side chains along the polypeptide chain and should the polypeptide chain be folded the polar groups would oppose each other in one fold and non-polar groups would oppose each other in the next fold. That may well be so for the soluble proteins but as the recent results obtained by Martin demonstrate, it does not apply to the polypeptide chains of wool. For if polar and nonpolar side chains alternate, no dipeptide consisting of two glutamic acid residues or of glutamic and aspartic acid residues should be possible.

Cystine, which is a di-alpha-amino acid, may be a part of two such chains, as was first suggested by Astbury and Street in 1931 (9). Other formulations in which the cystine is only partially built into polypeptide chains are unlikely. For if the cystine were a member of only one polypeptide chain processes that break the di-sulphide bond would result in elimination of half the sulphur. This does not occur. If either or both of the amino groups were uncombined, treatment of the wool with nitrous acid would destroy half or the whole of the cystine, whereas only a small proportion of cystine is destroyed by this treatment. Moreover there cannot be many free carboxyl groups since the free carboxyl groups in wool can be accounted for to a first approximation by its content of glutamic and aspartic acids. Such cross linking in which the cystine is a part of two polypeptide chains may account for the unusual insolubility of keratin protein and an analogy may be drawn with the solubility properties of cross linked thermo-hardening plastics, where increase of cross linking decreases the solubility.

Other possible cross linkages between polypeptide chains arise from the fact that some of the amino-acids are basic and others acidic. Aspartic acid is present in 100g. of wool according to Speakman and Townend (10) to the extent of 0.018gm. residues and glumatic acid to the extent of 0.0507 residues. (Astbury gives 0.0959 and 0.0494 gm. residues). From this total of 0.1587 gm. residues must be substracted the acid residues present as amides. Thus aspartic acid may be present as asparagine $H_2N.OC.CH_2CH(NH_2)COOH$ and glutamic acid as glutamine $H_2N.OC.CH_2CH_2(NH_2)COOH$. The amide nitrogen present in 100 gm. of wool is approximately 0.081 equivalents leaving 0.077 residues of aspartic and glutamic acids in which the terminal carboxyl group is free.

The basic amino acids, lysine, arginine and histidine, are slightly in excess of this and amounts to 0.819 residues. Should the acidic and basic residues be suitably placed in relation to one another salt formation may occur. These cross links are illustrated in Fig. I.

The presence of the basic and acidic residues in the ionised state as shown in the suggested model has been confirmed by measurement of the heat of reaction with hydrochloric acid. If the acid reacts with unionised amine, RNH_2, the heat evolution at room temperature is approximately 11,000 cals. per mol. If on the other hand it reacts with ionised carboxyl groups,

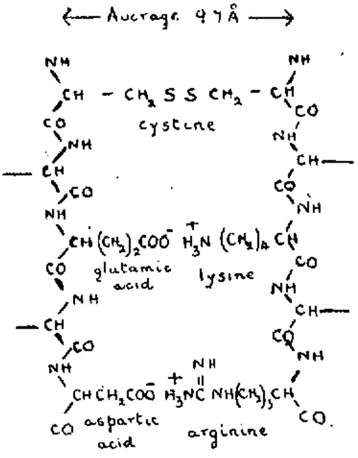


Fig I β keratin. Cystine and salt linkages (front elevation)

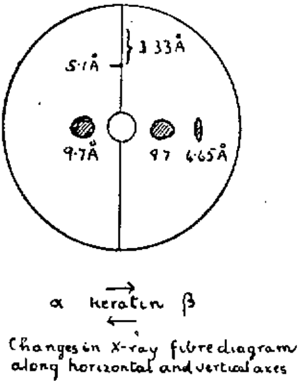


Fig. II

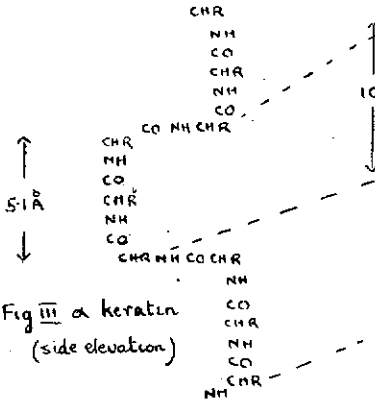


Fig III α keratin (side elevation)

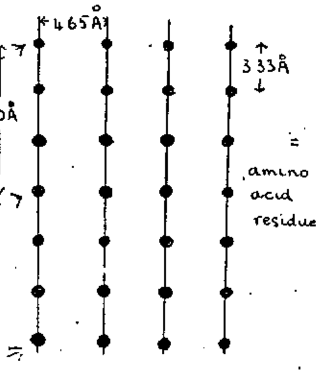


Fig IV Layers of β-keratin (side elevation)

RCOO—, the heat evolution is equal and opposite in sign to the heat absorbed when a carboxyl group ionises which is 1,000—2,000 cals/mol. Values of the heat change observed, vary from 2,000 to 3,500 cals/mol. evolved (12), which confirm the presence of the groups in their ionised forms RCOO— and RNH_3+ and the existence of salt linkages. On this view the groups present in the wool which combine with acid are the ionised carboxyl groups which, from the aspartic acid and glutamic acid content less the amide content, amount as we have seen to 0.077 equivalents/100 g. By titration of wool it is found (13) that 100 g, of wool combines with 80 c. cs. of **N**-hydrochloric acid, i.e., with 0.08 equivalents of acid: thus the analytical figures for ionised carboxyl groups deduced from amino-acid analysis, very nearly total the acid combining value of wool found by titration. The salt linkages appear to be reasonably well confirmed. Other cross links, in addition to those formed by cystine and by salt formation, probably exist due to hydrogen bonding.

This building up of the primary chemical structure was assisted considerably by the X-ray investigations of Astbury. In these well known investigations a homogenous beam of X-rays was directed at wool or hair fibre clamped with its axis vertical. Owing to the multitude of cortical cells lying with their long axis vertical within the fibre, the X-ray diffraction picture obtained resembles those in which a crystal is rotated about a vertical axis, for in the fibre, there will always be some of the crystallites correctly oriented to the beam and so X-ray diffraction will occur. The diffracted X-ray will reveal itself as spot or spots on a photographic plate suitably located at a distance behind the fibre. Using X-rays of constant wave length it is a simple consequence of the theory that the greater the displacement of the X-ray beam from its undeflected path, the smaller must be the distance between the reflecting planes. With the fibre vertical, spots on the equator of the X-ray photograph measure the spacing between vertical chains of atoms while spots on the meridian have reference to the vertical repeat pattern. The sharpness, or on the other hand, the diffuseness of the spot is well known to be an indication of the crystal size, for the smaller the crystal, with its fewer number of reflecting surfaces, the less sharply does it reflect and consequently the more diffuse is the reflected spot. Examination of the X-ray photograph of silk shows that there is in such fibres a definite horizontal as well as definite vertical pattern. Moreover, since the spots along the equator are much broader and diffuse than they are along the meridian, the photograph indicates that the reflecting crystallites are much smaller in a horizontal direction than they are in a vertical direction. Thus the physical picture of a silk fibre is of a number of long thin particles lying closely side by side and pointing along the length of the fibre. If the crystal particles pointed in all directions the resulting photograph would be a ring as occurs when a photograph is taken of a strip of photographic film which contains silver bromide crystals pointing at random in all directions.

The spacing of the vertical repeat pattern in silk fibre, obtained from the sharp line on the meridian, corresponds to $3.5A^0$ which is just the calculated distance for a fully extended amino acid residue. It would thus appear that the thin crystallites which lie along the silk fibre are composed of bundles of extended polypeptide chains. When wool is examined, the photograph shows, as does the silk fibre, a much sharper spot on the meridian than on the equator indicatinig long thin crystallites lying length-wise along the fibre. The vertical spacing is however quite different from that of silk and corresponds to a repeat at 5.1A°. When wool is stretched, however, the vertical repeat alters and occurs at 3.33A°, i.e., it corresponds to the repeat in an extended polypeptide chain. Unstretched wool, or alpha-keratin, thus undergoes a change in molecular folding on being stretched giving beta-keratin, and this change is a reversible one. The spot on the equator of the photograph of alpha-keratin corresponds to a separation of 9.7A° which has been identified with the lateral separation of the polypeptide chains. Thus if one likens the molecular model for wool to a ladder with cross links as rungs, the 9.7A° corresponds to the distance between the sides. Beta-keratin also shows the 9.7A° spacing, i.e., the distance between the sides of the ladder is not altered in the change from alpha to beta-keratin, but in addition a new spot has appeared indicating a spacing of 4.65A° as shown in Fig. II. This is identified as the thickness of the main chains which form the sides of the ladder when in their extended state. Thus the folding and unfolding of the polypeptide chains of wool in the alpha-beta transformation occurs in planes at right angles to the plane of the ladder. In order to accommodate the side chains and cross linkages of varying length the fold has been revised by Astbury and Bell in 1941 (26) following criticism by Newrath' of Astbury's earlier model. The side view of the ladder in its folded or alpha — form is shown in Fig. 3. The R groups, some of which will form cross links between neighbouring chains, are at right angles to the plane of the diagram and project alternately up and down.

The X-ray dimensions of beta-keratin, if the interpretation is correct, are those of an average amino-acid residue. Thus the mass of one residue = 9.7 x 4.65 x 3.33 x 10^{-24} x density. The density of wool = 1.3 gms/c.c. The average gram residue will be the weight of N average residues = 6.03 x 10^{-23} x 9.7 x 4.65 x 3.33 x 1.3 x 10^{-24} = 118. Therefore the number of gram residues in 100 gm. wool = 100/118 = 0.85 cf. 0.8597 found. Thus the amino acid analysis of wool is satisfactorily confirmed as complete.

This model of the wool crystallite lying with its long axis in the direction of the length of the fibre may perhaps be over simplified. Nevertheless it has provided a valuable working hypothesis and has offered an explanation of that very valuable property of the wool fibre, namely, its extensibility and permanent set.

When wool or hair is steamed and stretched at 100°, it is possible to obtain 100% extension. If the fibre is dried in this stretched state, it retains its extended form. This is termed temporary set, because when the fibre is wetted, the fibre contracts. If, however, the fibre is maintained in the stretched position for two or three minutes at 100° and then allowed to relax it shows super-contraction, contracting to a length less than its original length. Alternatively, if it is steamed at 100° in the stretched state for more than three minutes, it gradually acquires a permanent set. The fibre will not then contract even on boiling in dilute acid or on immersion in alkali.

According to Speakman, the reaction stage whch leads to supercontraction is the hydrolysis of the di-sulphide link between the polypeptide chains: $W\text{-}S\text{-}S\text{-}W + H_2O = WSH + WSOH$. The polypeptide chains are then free to fold up when the strain is removed, particularly if the lateral cohesion of the polypeptide chains is reduced by the intrusion of water molecules. If the extended fibre is steamed for over three minutes it is suggested that new bonds are formed between the terminal —SOH groups and free amino groups: $WSOH + H_2NW = WS.NH.W + H_2O$, which tend to fix the polypeptide chains in the extended state, so conferring permanent set. Supporting this view is the appearance and detection of free SH groups in the fibre after permanent set is conferred. Further, the amino groups would appear to be involved in the conferring of permanent set for if the wool is deaminated using sodium nitrite and acetic acid, permanent set is not possible. The new linkages which cause permanent set cannot be simply salt linkages or new di-sulphide linkages for both these are easily split by alkali or by boiling acid to which the permanent set is stable.

The nature of these cross linkages which confer permanent set is, hovever, still under discussion. The sulphenic acid, WCH_2SOH, formed by di-sulphide hydrolysis, may yield an aldehyde under alkaline conditions, liberating sulphide which can easily be recognised: $WCH_2SOH = WCHO + H_2S$. The aldehyde may condense with amino groups to give linkages of the type WCH:NW, but so far no products have been isolated from wool hydrolysates which contain this grouping. Consequently the existence of such linkages may be open to doubt. Horn, Jones and Ringel in 1941 isolated from alkali treated wools a new amino acid, lanthionine, having the formula, $HOOC.CH(NH_2)CH_2S.CH_2.CH(NH_2)COOH$, for which the following mechanism of formation appears likely (16), hydrolysis of the di-sulphide occurring, followed by $W.CHCH_2SOH = WC{:}CH_2 + H_2O + S$ and $WC{:}CH_2 + HS.CH_2CHW = WH.CH_2SCH_2.CHW$, giving lanthionine on hydrolysis. This is the only product isolated which is evidence for a new cross linkage brought about by simple treatment of the wool fibre. Its formation may play a part in the permanency of the set of an extended fibre.

Useful in the assessment of the degree of cross-linkage have been measurements of the work of extension of single fibres. This work of extension is obtained by plotting the standard load-extension curves and evaluating the area under the curve. Cross-linkage breakdown is attended by reduction in the work of extension. Thiol-acetic acid, $SHCH_2COOH$, is a reducing agent which reduces the di-sulphide group to two thiol groups, i.e., it breaks the di-sulphide cross-link and the result is a marked decrease in the work of extension.

$W\text{-}S\text{-}S\text{-}W + 2HS.CH_2COOH = WSH + HSW + (SCH_2COOH)_2$ Similarly in acid solution, the ionised carboxyl group is neutralised and the electrovalent salt linkage disappears. The extension of the fibre is therefore easier also in acid solution.

Reduced wool containing free —SH groups may react with alkyl halides (17) to give chemically modified wool: $W\text{—}SH + RX = W\text{-}S\text{-}R + HX$. Dihalides are also capable of reacting with reduced wool forming new cross links in which the sulphur atoms of the cystine are connected by short hydrocarbon chains.

$2W\text{—}SH + (CH_2)nX_2 = W.S\text{-}(CH_2)n\text{-}S\text{-}W + 2HX$. Reduced wool treated by dihalides such as ethylene dibromide has a work of extension and breaking strength not far different from that of untreated wool, whilst reduced wool or reduced and methylated wool has a work of extension about two-thirds that of untreated wool. The formation of these new cross links by the action of dihalides confers increased alkali resistance and renders the wool, as was shown by Harris and co-workers, resistant to moth attack. This is but one of the many methods of rendering wool resistant to moth attack but is one especially interesting in that the digestive system of the moth larvae, whilst capable of splitting the disulphide bond, cannot apparently split the more stable thio-ether linkages in this chemically modified wool.

Much work has been done on the mechanism of the permanent set of keratain fibres, and its importance in the technology of finishing of wool fabrics is considerable. In view of the heterogeneous nature of wool it is of interest to note that the property of super-contraction and of set has been connected by Woods (18) in 1938 with the cortical cells. Woods separated cortical cells and by appropriate treatment was able to cause them to super-contract and also to assume both temporary and permanent set. A similar conclusion has recently been reached by other workers (19).

Some reference must now be made to work which has been carried out on wool with a view to prevention of shrinkage. From the textile point of view, shrinkage or felting is of course one of the very valuable properties of the wool fibre for it allows of the production of cloth in which the separate fibres have become interlocked giving a uniformity of surface, in which the spaces between the yarns have been eliminated. The technological problem is to utilise this beneficial property where needed and to control it where it is disadvantageous. An illuminating experiment is to tie a staple of greasy wool in the middle and then wash or "scour" it. The portion towards the base felts rapidly whilst the portion towards the tip which is free from root ends remains unfelted. Felting is caused by the migration of the fibre in the direction of its root end. The surface friction of the fibre can be measured in various ways (20) and it is less from root to tip than it is in the opposite direction. This has for a long time been attributed to the scale structure of the fibre and the scales have been assumed to exert a ratchet and pawl action. The electron microscope indicates this physical structure very clearly and the way the scale edge is rounded off in certain anti-shrink treatments. This difference in friction with and against the scales correlates with the ability to felt as recognised in practice and until recently all anti-shrink treatments have resulted in reducing or eliminating this directional frictional effect.

The common anti-shrink treatment is with a solution of hypochlorite or with aqueous or gaseous chlorine. Recently with Miss R. Mauger, a New Zealand Wool Board Research Fellow at the University of Otago, an attempt is being made to elucidate more fully the chemistry of wool chlorination. The method of approach has been to examine the separate amino acids after protection of the amino groups by acetylation. It is, of course, recognised that bi-molecular reactions are possible in solution which could not occur in a rigid structure owing to spatial considerations. Hypochlorite solutions react with amide groups and with the guanidine portion of arginine to form chloroamines. The reaction with a substance such as methyl guanidine is very fast and as in certain other cases investigated the reaction involves the hypochlorite ion. In acid solution this reaction rate decreases as the ionisation of the hypochlorous acid decreases. The oxidation of diacetyl cystine is also a very fast reaction, apparently involving the unionised hypochlorous acid, but in buffered solutions the rate depends to a marked extent at constant pH on the nature and concentration of the buffer solution. The end product of the reaction appears to be acetyl cysteic acid. Taking 1 mol. of diacetyl cystine and 8 mols. of hypochlorous acid, 5 mols. of hypochlorous acid are rapidly used up, a further 2 mols. form chloramides by reaction with the NH.CO groups present, leaving 1 mol. of residual hypochlorous acid. Simultaneously the acid titre increases by 7 mols. i.e., by 5 mols. of hydrochloric acid and 2 mols. of acetyl cysteic acid.

Cysteic acid has also been found in wool hydrolysates after chlorination and there appears general agreement that the splitting and oxidation of the di-sulphide bond is an essential part of many non-shrink processes. The production of the strongly ionised sulphonic acid groups on the surface of the wool cause gelatinisation of the surface by swelling. When wool is immersed in chlorine water, there are sacs formed along the surface of the fibre. This is the Allworden reaction (21) and may be explained by the diffusion of chlorine through the k_1 layer which contains little or no cystine followed by reaction of chlorine with some of the cystine of the k_2 layer to form cysteic acid. Cysteic acid side chains ionise and give a Donnan equilibrium effect of excess diffusible ions inside the k_1 layer with consequent swelling. Surface swelling and gelatinisation will remove the directional frictional effect and thus provides an explanation of the shrinkage resistance. In acid solution, where the excess of diffusible ions inside the surface layer is reduced, swelling will be minimised and shrinkage may still occur even when it does not occur in mildly alkaline soap solutions.

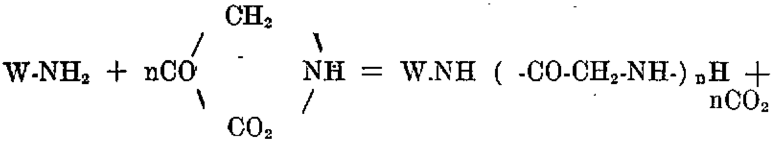
According to Phillips (22) who has recently divided the combined cystine of wool into 4 fractions, A, B, C and D, which differ in reactivity and mode of reaction with alkalies and other substances, it is the (A + B) cystine fraction which appears to be concerned in shrinkage properties. The (A + B) fractions amounting to 50% of the total cystine are converted by alkalis to lanthionine in a way already indicated. Wools which have been first treated with alkali and subsequently chlorinated do not acquire shrinkage resistance. This suggests that the cleavage and oxidation of the (A + B) cystine is an essential step in destroying the felting power of wool.

The explanation advanced for the differences in behaviour of the 4 fractions of combined cystine is that they arise through variation in side chain environment and there is some evidence that the (A + B) fractions are associated with an environment of polar side chains whilst C and D are associated with non-polar chains.

Chlorination by gaseous chlorine (27) provides a more uniform treatment than wet chlorination. The latter tends to cause over treatment of the more accessible fibres. This method of dry chlorination to-day may be followed by the action of papain leaving a wool which is scaleless, though the fibres are otherwise intact. The wool is soft and possesses a silk-like gloss and is completely non-feltable. It is so completely non-felting that it may be used as a filling for washable quilts and cushions.

So far it is the directional frictional effect which has been emphasized. However, in order that felting may occur, the wool fibre must be able to extend and to contract after extension. Consequently unshrinkability may be realised by increasing the resistance of the fibre to extension or by decreasing its power of recovery. This has been achieved by Barr and Speakman by increasing the number of cross-linkages between the peptide chains (23). Mercuric acetate and benzoquinone have been used for this purpose. Although the frictional properties of the fibres were unaffected, a high degree of unshrinkability was obtained by such treatment.

Another method of approach has been made by Speakman (24). This consists in building up a film of polymer on the reactive side chains of the wool using suitable monomers and so masking the scale structure. Anhydrocarboxy glycine appears to be particularly suitable in this connection for the polymerisation is initiated by water and the film produced is protein-like in character.



$$W\text{-}NH_2 + nCO\begin{array}{c} CH_2 \\ \diagup \qquad \diagdown \\ \\ \diagdown \qquad \diagup \\ CO_2 \end{array}NH = W.NH\,(\,\text{-}CO\text{-}CH_2\text{-}NH\text{-})_nH + nCO_2$$

Since the film is protein-like the fibre should retain the characteristic properties of wool apart from its ability to felt. A noteworthy result of this treatment is increased abrasion resistance, addition of 4 per cent. of anhydro carboxy glycine conferring an increased wear resistance of 300 per cent.

I would like in conclusion to refer to one other physical property of wool, namely, its equilibrium with water vapour. Fabrics made up of fine fibres expose a large surface to the air and consequently come very rapidly to equilibrium with the air in their immediate vicinity. A loose yarn, and a loose yarn is characteristic of wool, obviously presents more surface than a yarn which is tightly twisted. The surface of 1lb. of wool is easily calculated knowing the density of wool and the diameter of the fibre. Taking 1lb. of a fine wool, such as 64's quality of diameter of 20 microns, the area of the fibres is 800 sq. ft. A suit usually weighs about 3 lbs. and represents a fibre surface area of 2,400 sq. ft. This large area means a rapid reaction to any change in atmospheric humidity. This, however, does not mean that a mass of wool rapidly comes to equilibrium with surrounding air, for the surrounding air takes time to displace the air entrapped by the wool and what is termed conditioning is a slow process. Wool may absorb up to 33% of its weight of water and to a first approximation the water absorbed is dependent on the relative humidity of the atmosphere. The curve obtained by plotting water absorbed against relative humidity is only slightly dependent on temperature. Thus the effect of temperature on the water absorbed may be deduced from the changes in the atmospheric relative humidity.

The actual amount of water vapour in the air in a well ventilated room is the same as it is out of doors, i.e., the absolute humidity is approximately the same, but since a room in winter is heated, the relative humidity of the air inside is much less than outside. A suit containing 3lbs. of wool if in equilibrium with typical indoor conditions in winter would absorb roughly ½lb. of water if allowed to recondition out of doors. The heat evolved when ½lb. of water is absorbed by wool is 600 B.T.U's which is as much heat as a man's body normally generates in 1½ hours. This remarkable evolution of heat is a great protection against the temperature drop on proceeding out of doors, particularly if the heat is liberated gradually. It is important that the heat be evolved at a suitable rate for it would be useless if liberated immediately or too slowly. If at constant absolute humidity the temperature of the air is reduced, its relative humidity is increased, water is absorbed and both fabric and the entrapped air are warmed. This heat may be radiated, or entrapped air may be replaced by other air. Thus the rate at which heat is given up depends partly on the rate of passage of air through the fabric. The more rapid the passage of air through the fabric, and the more likely the sensation of cold, the more rapidly is heat generated. So long as the fabric is absorbing water from the perfusing air, the air and fabric will be warmed. Looked at from another viewpoint: the percentage of water in the fabric will change only slowly, because the fabric contains so much more water than a corresponding volume of air. The water content of the air in the fabric is controlled by the water content of the wool. Hence a conditioned fabric will tend to keep any air passing through it, at the relative humidity at which it was conditioned. Thus if the fabric is conditioned, i.e., is in equilibrium with air, at an indoor temperature of 65° and a relative humidity of 45%, and cold air at 40° and relative humidity at 95% is then blown through the fabric, the air must emerge at the original relative humidity of 45%. Since some of the water in the air is removed by the wool, the air reaches the relative humidity of 45% at a temperature intermediate between 65° and 40°F. The method of calculating this temperature was due to Cassie (25) in 1940 and has been shown to agree well with experiment. In the case considered the cold air by passing through the wool is warmed to about 52° approximately half-way between the indoor and outdoor temperatures. Obviously the greater the amount of water which can be taken up as the relative humidity of the atmosphere increases, the longer can the fabric give out heat and afford protection. From this angle wool is in an advantageous position as a textile fibre.

It is interesting to note that if wool be conditioned indoors at 65° in a badly ventilated room where the relative humidity is high, removal of the wool to a cold outdoor temperature at the same relative humidity will not be attended by any further absorption of water vapour and consequently heat will not be generated; under such conditions the heat-generating properties of wool are in abeyance.

In this address I have attempted to bring together some of the advances which have been made in our knowledge of the wool fibre and to indicate the lines along which advance has occurred. The study of a particular problem frequently leads to results which illuminate a wider field, and the investigation of wool fibre is an example of this. From a study initiated by technological considerations, new chapters have been added to the chemistry of proteins and the essential similarity of the protein of wool fibre, the myosin of muscle, and also of soluble protein after denaturation has been discovered. The study of the wool fibre is proving a valuable bridgehead to that still largely unknown country of protein chemistry.

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CONFERENCE, 1947.

The Annual Conference, held as a part of the Sixth Congress of the Royal Society of New Zealand, gave evidence of the progress of all branches of New Zealand Chemistry. The Presidential address was held as one of the major evening sessions of the congress, and was attended by many members of the participating bodies other than chemists. Professor Soper's review of the contributions physical science has made to one of our basic industries was, without doubt, one of the highlights of the congress.

Many chemists were to be seen at sessions other than those of Section B. Nevertheless the Joint Institutes' own sessions were loyally supported. Chemists are especially grateful to Mr. I. D. Dick, whose introductory paper to the Second Industrial Session, on "Statistical Method in Chemical Research," provided, not only an interesting historical account of the introduction of such methods into industrial research, but also a clear and simple account of how the methods can be used in routine analysis.

PERSONAL

DR. R. A. ROBINSON

The resignation of Dr. R. A. Robinson from the post of Associate Professor of Chemistry at Auckland University College, brings to a close a period of fruitful teaching and research in physical chemistry. Dr. Robinson graduated from Birmingham University and went as a Commonwealth Fellow to the laboratory of H. S. Harned, first at Pennsylvania and then at Yale. At this period Dr. Robinson was associated with the early development of Harned's accurate methods of determining the thermodynamics of ionic solutions by galvanic cells, which have greatly increased precision in such measurements. After a short time at Exeter, he came to Auckland in 1933. At that time D. A. Sinclair had established the conditions needed to make the "isopiestic" method of comparing the vapour pressures of aqueous solutions, a precision method. Robinson immediately applied it to the determination of the variation of the partial free energy of ions with concentration, and in the following years, produced a large amount of data of high accuracy covering a wide variety of salts. In this work he was assisted by a number of able students, outstanding among whom is R. H. Stokes, whose own contributions to the field of electrolytic solutions have been recognised by awards, successively, of the Rennie Medal (Australian Chemical Institute), Meldola Medal (Royal Institute of Chemistry), a Commonwealth S.I.R. Fellowship and recently an I.C.I. Fellowship at Cambridge University. If it is reasonable to claim, as O. Redlich has done (Chemical Reviews, Vol. 39, No. 2, 1946) that the problem of the dissociation of electrolytes, the classical problem of physical chemistry, is on the way to being solved; the contribution of Robinson and his collaborators is a significant one.

During his term in Auckland, Dr. Robnson travelled abroad to England in 1936, to Yale as Sterling Fellow in 1940, and again to Canada where he was in charge of a chemical warfare research station for over two years. He has returned now to England to join the staff of the Courtauld Institute of Biochemistry. New Zealand chemistry can ill afford to lose one of its leaders in fundamental research, or the New Zealand University a teacher who has stimulated so many students.

Mr. R. H. Stokes will represent the Institute at the Perth meeting of the Australian and New Zealand Association for the advancement of science. He will deliver a paper on "The Thermodynamics of Ionic Hydration."

Mr. A. I. Biggs, Associate, has been transferred from West Africa to the Malayan Chemical Service, a part of the Unified Colonial Chemical Service.

TO YOUNG CHEMISTS WITH UNIVERSITY DEGREES INTERESTED IN EXPERIENCE ABROAD.

Chemists with University degrees who are interested in spending at least five years in the chemical industry in the United Kingdom are invited to make application. Selected applicants will have their passages paid to and from the United Kingdom and their commencing salary will be between £350 and £450 sterling, according to qualifications, post graduate work, etc. Apply, with copies of testimonials to G.P.O. Box 1486, Wellington.

PER ANGUSTA

With the fuel shortage rife, the chemist's life
Is marred by frustration of toil;
But what of the life of the chemist's wife,
Who must see her dinner spoil
While, cursing his fate, her harassed mate
Works on for an extra hour,
Watching stills that are slow when the gas is low
And there's no electric power,
Or straining his sight by candlelight
Trying to read a burette!
Back in the house, the chemist's spouse,
With the very same power cuts beset,
Tries to keep the meal hot by putting the pot
At the side of the sitting-room fire
And risks, should it spoil through too long a boil,
Incurring her husband's ire.
So if you are prone the mess to bemoan
That shortages make of your life,
As your whole being inner appreciates dinner
Pity the lot of your wife!

M.P.B.

BOOK REVIEW.

SOME BOOKS ON PHYSICAL METHODS IN GENERAL AND ANALYTICAL CHEMISTRY.

In recent years some physical methods have proved of such value that units of apparatus have become commercially available for their execution. As a result many laboratories find that they have instruments in their possession whose entrails are a mystery — indeed it is almost a point of salesmanship that the instrument can be used without understanding its construction or the relevant theory. The high price and lack of standardisation of the parts is usually a sufficient deterrent to the chemist with an enquiring mind and a screwdriver.

The glass electrode pH meter is a case in point. To have read Malcolm Dole's lucid and scholarly account of this instrument (M.Dole "The Glass Electrode" Wiley, 1941) is to view with opened if jaded eye the results of pH measurements with commercial instruments that are reported in the literature. The study has its positive advantages. A study of the electrical circuits will show that the electronic nullpoint apparatus and potentiometer that are part of most pH-meters is a far more satisfactory device for potentiometric titrations than the usual galvanometer. The possibilities of pH meters in this direction are seldom fully exploited. Kolthoff and Laitinen's "pH and

Electro Titrations" (Wiley, 1944) is helpful here. It is a book for student use in a practical course and in consequence the apparatus described therein may be expected to be robust, inexpensive and reliable.

The pH meter may also be used as a current measuring device of sensitivity comparable with a high class of galvanometer. It serves excellently in this connection as the basis of a polarograph. No chemist for whom microanalysis is important can afford to be unaquainted with the scope of polarography. Kolthoff and Lingane, "Polarography" (Interscience, 1941) will provide the information.

The speed anad accuracy of photoelectric colorimetry has caused a recent influx of photoelectric colorimeters and spectrophotometers into N.Z. laboratories. They are well discussed in "Optical Methods of Chemical Analysis" of T. R. P. Gibb, (McGraw-Hill, 1942) in which one may also find a section on the use of the polarising microscope—an instrument whose versatility seems to be better appreciated by geologists than by chemists. Not many chemists will have apparatus at their disposal for emission spectroscopy. For those seeking an introduction to the practical and empirical aspects of this subject adequate for analytical purposes, W. R. Brode "Chemical Spectroscopy" (Wiley, 1943) is a good book. It contains a valuable compilation of spectra as an appendix.

There is a serious need for a book to guide the chemist who for financial reasons is lucky enough to be forced to make his own apparatus. Strong, J. "Procedures in experimental physics" (Prentice-Hall, 1945) is helpful on the technical side, and much information of a scattered nature is available in the periodicals. To make relays, amplifiers, detectors, oscillators and the like an elementary knowledge of radiophysics is needed but the reviewer is not competent to recommend books in this field.

Chromatography is becoming part of the stock in trade of organic chemists. The subject is developing so rapidly in both practical and theoretical aspects that the two recent monographs on the subject (Zechmeister and Cholnoky "Principles and Practice of Chromatography" (Chapman-Hall, 1941) and Strain, H. H., "Chromatographic Adsorption Analysis" (Interscience, 1945) are already out of date. Neither treat adequately the important practical advances of partition and displacement chromatography, or the theoretical relationship between adsorption isotherms and chromatographic behaviour. If funds are slender it might be wisdom to wait a while for a new book.

A recent and most important addition to the literature of physical methods is Weissberger, (ed.) "Physical methods of Organic Chemistry," (Interscience, 1945). The list of contributing authors includes L. O. Brockway, K. Fajans, I. Fankuchen, W. D. Harkins, H. Mark, L. Michaelis, T. Shedlovsky, C. P. Smyth, and W. Swietoslawski. The matters discussed include, among others, melting and boiling points, surface properties of liquids, microscopy, crystal form and analysis, spectroscopy and colorimetry, polarography, potentiometry and conductivity, and fluorimetry. The more complex techniques, including the use of radioactive and isotopic indicators sound engagingly simple in the words of experts. The chapters on X-ray and electron diffraction and mass spectrometry should prepare N.Z. chemists for the day when this type of apparatus will become more readily available. It is a pity that chromatography does not find a place.

The material in the two volumes is of a uniformly high quality, though two of the chapters suffer in the presentation. It is a pity that one of these is on potentiometry. Kolthoff and Laitinen's book will partly bridge this gap. References to the literature are full. The reviewer has found them most useful in finding information on the construction of apparatus. Many of the chapters are preceded by a concise account of the relevant theory and scope of the method in organic chemistry.

The whole compilation makes stimulating reading and is a reliable reference book in time of need.

W.S.M.

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BRANCH NOTES

AUCKLAND BRANCH

At the April meeting Dr. Marsden addressed a public gathering on "Atomic Energy and its Implications."

Dr. Marsden introduced his subject with a discussion on the various atomic particles and showed slides depicting a physical concept of their arrangement within various atoms including a description of isotopes. He then went on to the postulates of Einstein regarding the conversion of mass into energy and showed its relation to spontaneous radio-activity. The difference between spontaneous radio-activity and the fission of heavy atoms to produce atomic energy was then described and the case of Uranium of atomic weight 235 cited giving Krypton, Barium and neutrons. Dr. Marsden then dealt with the use of moderators to slow down the neutrons generated in an atomic pile for the production of heavy atoms and mentioned the use of graphite and heavy water for this purpose. He then described the various methods of separation of U235 from U238. Dr. Marsden closed with a talk on the implications of the release of atomic energy, the absolute necessity for an efficient means of control of such energy and of the grave responsibility which rests on the shoulders of present and future scientists to see that mankind is not exterminated from the face of the earth in an atomic war.

Dr. L. Brown M.D., of the Pathological Dept., Auckland Hospital addressed the May meeting on "The Identification of Fire-arms."

It may be questioned why a medical man, even one trained in Forensic Medicine, should consider it necessary to acquire a knowledge of ballistics; for it cannot be claimed that a medical training is essential to understand the mechanism of action or the principles of identification of a particular fire-arm. In most countries including New Zealand there are highly skilled official ballistics experts whose knowledge may be utilised in any legal case involving firearms. However valuable this knowledge may be in cases involving injury to the body, invariably there remains to be answered questions requiring medical knowledge as well.

For instance, the identification of a firearm wound as such is not always as simple as it seems, for many firearm injuries bear little resemblance to the common ideas of what such injuries should be. Other questions include some indication of the type of weapon and projectile used, the distance or range and the number of shots fired. It is of obvious importance to ascertain whether one is dealing with a case of accident, suicide or murder, or was the wound self-inflicted for the purpose of deceit or malingering, and what volitional acts if any were possible after infliction of the injury.

The appearances of a firearm injury cannot be fully understood without an elementary knowledge of ballistics. The charge upon ignition liberates a considerable quantity of gas under extremely high pressure which forces the projectile from the muzzle of the weapon. With the projectile there are included the products of combustion such as flame, smoke, gas and particles of burned and unburned powder. At point blank and short ranges all these factors are recorded on the body, and from their distribution and appearance we may deduce facts of importance. Beyond a few feet the projectile, having outstripped the other components, produces a rather distinctive entrance wound, which must be distinguished from the often less distinctive exit wound. With high velocity bullets such as those used in the ordinary Service rifle, the effects up to 200-300 yards range may be explosive in character and cause pulping of the tissues over an area of about 6—9 inches. The results of experimental work in connection with the cause of this bizarre effect lead one to the opinion that when such a bullet, travelling at almost 3,000 feet/sec. at about 3,000 revs/sec., meets any resistance its energy is converted into work which is imparted to the tissues struck thus causing gross destruction.

The projectile, cartridge case and particles of burned and unburned powder may all contribute to the identification of the weapon used. During its forced passage through the barrel, the bullet becomes marked with grooves imparted to it by the rifling in the barrel and scratched by fouling and imperfections. Similarly the mechanism of loading and extraction, particularly in automatic weapons, often imparts individual characteristic marks on the cartridge case. With ignition of the charge the expansion is in all directions and the lateral component may cause imperfection of the firing chamber to be imprinted on the sides of the cartridge case; and, similarly, the force backwards may cause marks on the breech face to be recorded on the soft percussion cap. The striker pin may also make its distinctive mark.

In illustration of all these points, Dr. Brown utilised lantern slides of photographs from cases in which he participated and from cases which constitute the unique collection and experience of Professor Sydney Smith, Professor of Forensic Medicine at Edinburgh University.

The Branch is now subscribing to and circulating to members the following journals: the Journal of Chemical Education, the Analyst, and the Industrial Edition of the Journal of the Indian Chemical Society.

WELLINGTON BRANCH.

At the May meeting of the Wellington Branch three speakers read papers on "Some Modern Analytical Techniques."

1. Mr. I. S. Hunt, of the Dominion Laboratory spoke on "Electrolytic Methods of Analysis."

The special value of electrolytic methods in the analysis of metals lies in the ease with which rapid and quantitative separations may be made from a single solution. These involve a minimum of handling and often the elimination of unpleasant and tedious manipulations which would be necessary with chemical methods. These advantages are still more in evidence in analysing non-ferrous alloys where many of the constituent metals are reasonably well separated in the standard potential series.

The key to the electrolytic separation of a number of metals in solution lies in the relative values of their standard electrode potentials.

By means of Nernst's expression

$$E = E_0 + \frac{RT}{NF} \log_e a,$$

variations in equilibrium potential with ionic concentration, ionic valency, and temperature were illustrated. In this way it is possible to predetermine the potential relationship in a solution being analysed, and thus control the deposition of metals present.

The method of separating a number of metals by electrodeposition was explained. The metals most commonly encountered in metal analysis are divided into groups according to their position in the standard electrode series. In general, metals in different groups have sufficient difference of potential to allow separation by controlling the cathode/catholyte potential. In order to separate metals within the same group other means have to be employed, e.g., the use of complex ion formation on the anodic deposition of a metal as peroxide.

A demonstration was given of equipment in use at the Dominion Laboratory, and of typical methods for analysing non-ferrous metals.

The speaker concluded by discussing schemes for the complete analysis of brass, bronze, bearing metals, aluminium alloys, and low melting point alloys, using controlled potential technique.

2. Taking the subject "The Identification of Material by the Hanawalt X-Ray Diffraction Method," Mr. R. J. Munster of the Dominion Laboratory said that the basic technique of this method was not discovered by Hanawalt although it bears his name because he indexed 1,000 compounds according to their X-ray diffraction patterns.

Soon after Von Laue's discovery, in 1912, that crystals could be used as three dimensional gratings for diffracting X-rays, Bragg developed his ionization spectrometer along with a simple theory of X-ray diffraction. In both these methods a single, relatively large, oriented crystal is used giving a number of diffraction spots on the film—although the patterns are unique for each crystal it would be very difficult to index any such pattern.

Hull, in America, discovered the powder method of X-ray analysis in 1917, almost simultaneously with Debye and Scherrer in Europe. In this method the specimen is powdered and mounted in the centre of the camera round the outside of which the film is wrapped concentric with the specimen. The X-ray beam is defined by three slits, filtered (for instance radiation from a copper target is filtered with nickel) and then impinges on the specimen and due to the random orientation of the small crystals the spots of the single crystal method give way to diffraction circles concentric with the incident beam of X-rays. This results in a very great reduction in exposure time and a much clearer pattern is also obtained.

The "d values" or interplanar spacings are calculated from the diameters of the diffraction rings on the films and by using the Bragg formula—these and the relative intensities are noted for each line. Use is made of the three brightest lines to index the patterns in card form—three cards appearing for each substance, one with the brightest line first, one with the second brightest, and the other with the third brightest line first. The cards are listed in the order of "d value" appearing first on the card. The card on which the brightest line is listed first bears the complete pattern plus any relevant crystal structure which may be known.

3. Dealing with "Colorimetry," Mr. G. D. Gemmell of the Soil Bureau briefly reviewed the fundamental principles upon which colorimetric analysis is based and discussed methods of measurement, with particular reference to the type of electrophotometer used at the Soil Bureau, and considered the possible errors involved in analysis using such an instrument.

He said that chemical colorimetry implies a determination of the concentration of a coloured solute by measurement of the relative absorption of the solution. For this to be possible the relationship between solute concentration and relative absorption must be known, and this is given in the Beer—Lambert Law. The present trend towards the increased use of electrical instruments for chemical analysis is evident in the field of colorimetry, and many different types of instruments are to be seen in the literature. The advantages of these instruments are—

(1) A greater acuracy because of the objective nature of the reading.

(2) A reduction of fatigue in a series of measurements.

(3) Greater speed of working.

Photo-electric colorimeters employ either the photo-electric cell or the photo-voltaic or barrier layer cell; each has its advantages and its specific applications for which it is best suited.

The response of most Photo-electric devices is not uniform over the entire active area, and it is therefore, important that exactly the same region be illuminated every time. A diffusing screen placed in front of the element will eliminate variations, from this source.

It may be shown mathematically that errors in setting the zero point (point of zero transmission) and the point of zero concentration of the solute, also in reading the galvanometer deflection for transmitted light, produce high relative errors when a photo-electric photometer is used with solutions of high or low absorption. For maximum accuracy, conditions should be so chosen that readings of transmitted illumination fall on the central portion of the scale.

Mr. Gemmell illustrated his paper very fully with slides and delivered his lecture chiefly on points shown therein.

On June 4th, Mr. G. A. Lawrence spoke on "Some Aspects of the Biochemistry of Malting."

The sprouting of grain, as a prelude to production of sugar for fermentation to alcohol is a very ancient process but there are no definite records as to how, when and where it first originated. Beer was a common beverage in Ancient Egypt and as at that time it was a great grain growing country it is reasonable to assume that the chief fermentable materials were obtained from grain, indeed a method of making beer is described in several Egyptian papyri; it consisted of moistening the grain and allowing it to sprout, it was then ground, moistened with water formed in lumps and lightly baked to a sort of bread, the insides of the lumps remaining somewhat raw, This bread which must have been very akin to malt, was broken into pieces and allowed to ferment in tubs.

The modern method of preparing malt is to steep the grain in water, spread the moistened grain on floors, where it is allowed to germinate. In order to assist aeration the sprouting grain is forked and raked at intervals. When sprouting has reached a certain point as shown by the development of roots and acrospire the grain is allowed to wither. From the floors the grain is loaded on to the kilns where it is subject to gradually rising temperature until the moisture content of the resultant malt is reduced to about 2 per cent.

It is during this process of germination that the enzymes are produced or liberated. By means of tables and analytical data the speaker illustrated the development of the enzymes and the biochemical changes they produced in the grain. Ungerminated barley contains small quantities of enzymes in the free state but as germination proceeds enzymes in the combined or inactive state are released.

Proteolytic enzymes of the types protinases and peptidases have been found in green malt. The protinases appear to be responsible for the hydrolysis of barley proteins such as Nordein and glutelin to produce the noncoagulable proteins in the finished malt. They are also responsible for the liberation of diastase. The dipeptidases are thought to be responsible for the production of certain of the amino acids which are perhaps the chief sources of nitrogen supply to the yeast during fermentation of the worts. There are two types of starch splitting enzymes in malt; A—amylase has been called the dextrin forming amylase because it splits the starch molecule into large fragments but only produces a limited quantity of maltose. When a-amylase alone acts on soluble starch the liquid ceases to give a blue colour with iodine when only 11% of maltose is formed. B-amylase on the other hand attacks the linkages in the starch molecule in such a manner that maltose predominates. The products of hydrolysis of starch by b-amylase is 60% b-Maltose and 40% a-Dextrin. The latter is of such molecular weight that it still gives a blue colour with iodine.

Other enzymes which play an important part in the production of malt are cytase which hydrolyses the hemicellulose walls of the starch containing endosperm cells and so allows the passage of protein and starch splitting enzymes. Phosphatase also plays a part in the splitting of phosphorus from such organic phosphorus compounds as phytin. These liberated phosphorus compounds play an important part in subsequent mashing and fermenting.

The speaker pointed out and illustrated by analytical figures that production of sugar by hydrolysis of starch during the actual process of malting is comparatively small. The main object in malting is to allow the germination processes to proceed to such a point that adequate production of enzymes results and that during this process and the subsequent kilning there would be proper hydrolysis of proteins coupled with breaking down of the cell walls of the endosperm where the reserve starch is stored. It is during the mashing process where the malt grist is treated with water that the amylases do their main work in hydrolysing the starch to sugars, and it is here, owing to the fact that a- and b-Amylase have different optimum temperatures that the brewer is able to exercise some control on the sugar-dextrin ratio of the resultant worts.

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CANTERBURY BRANCH.

A joint meeting of the Canterbury College Scientific Society, and the Canterbury Branch of the Institute, was addressed by Dr. B. H. Mason on "X-rays in Industry." Dr. Mason, who is a graduate of Canterbury College in chemistry and geology, has accepted an appointment as Professor of Mineralogy at the University of Indiana.

After outlining the methods used for studying X-ray diffraction by crystals, the Lauve method, the Bragg spectrometer method, the rotating crystal mehod, and the powder method, the speaker gave examples of the industrial application of the last named method.

In the industrial laboratory, it may be desirable to know what compounds are present in a given material, while chemical analysis will give only the constituent elements and not their state of combination. Thus the distinction between a simple mixture and alumina and cilica, and the compound mullite formed on heat treatment at high temperature is almost impossible by normal chemical means, but completely different x-ray patterns are obtained. Identification of unknown substances is achieved by comparison with photographs of known pure substances. An index has been prepared giving the positions of the three strongest lines of all published powder photographs. This index, which already covers 4,000 substances, is of considerable assistance in routine identification.

In mixtures, each substance gives its own pattern of lines, with intensities proportional to the amount of the component. This allows for quantitive estimation, though the accuracy is not high. In a favourable case, it was possible to recognise 1% Mn_2O_3 in Fe_2O_3. Differentiation between compound formation, solid solutions and mixtures is possible, and the application of powder photography to the study of polymorphisim has resulted in the elimination of a great number of supposed polymorphic forms, and the discovery of unsuspected genuine examples. An important industrial application is in the field of refractories e.g., silica bricks. To produce good quality bricks, at least 95% of quartz should be converted to tridymite and cristobalite. In the paint industry, rutile is the best form of TiO_2 for a pigment, and its production is best controlled by x-ray examination. Grain size, in the range from 0.00001 cms to 0.0000001 cms, can be estimated.

Dr. Mason finally outlined some work which he carried out in Sweden on the occurrence of Fe_3O_4 in Mn_3O_4 ores. Synthetic preparations of the mixed oxides were studied from pure Fe_3O_4 to pure Mn_3O_4. Mn atoms can replace Fe atoms up to 60% without change in the pattern of lines, though a regular shift in their position showed an expansion of the lattice necessary to accomodate the larger Mn atom. At 65% Mn a fundamental change occurred, indicating a lowering of the crystal symmetry from cubic to tetragonal. The new pattern persisted to pure Mn_3O_4, and estimation of the composition of an unknown mixture to within 2% was possible.

The Institute as a whole is not responsible for statements and opinions appearing in this Journal.

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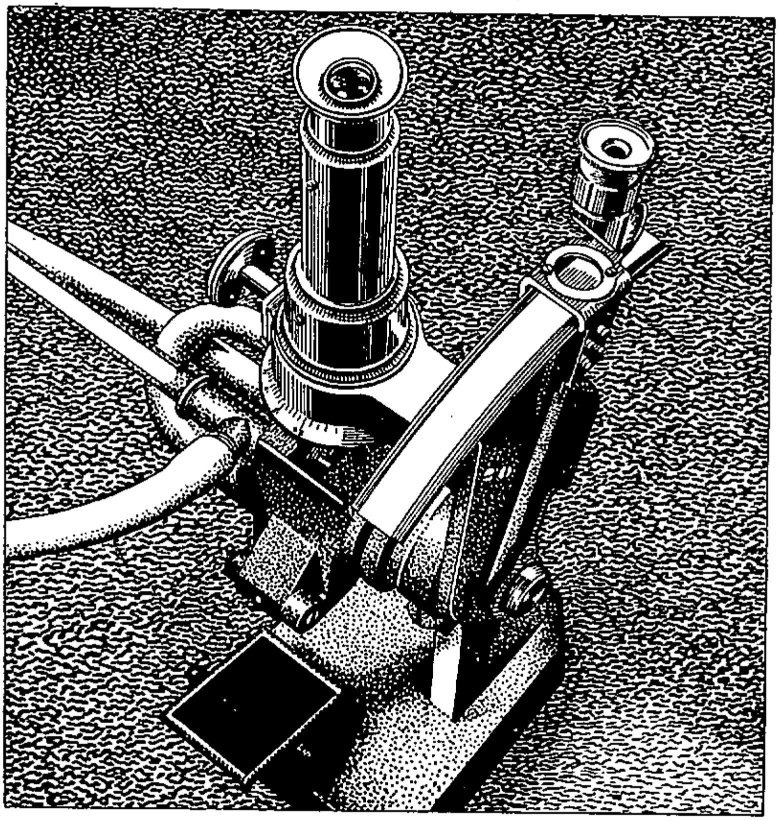
Crooked Sticks



This is a refractometer. Thrust a straight stick into water and it appears bent. Something really is bent, but it is not the stick. It is the light rays reflected from the part of the stick under the water. When light rays leave the surface of water, or any other transparent liquid, they bend at an angle which differs for various liquids. The amount of bending is known as the "refractive index" and can be measured by means of the refractometer. The refractive indices of nearly all pure transparent liquids are accurately known, but the presence of any impurity alters them. Because it quickly detects these alterations, the refractometer affords a reliable method of testing for purity. If the liquid under examination is known to be pure, the instrument can be used just as easily to discover or confirm its identity. The refractometer is widely used in the chemical industry whenever transparent liquids are concerned. Explosives, for instance, are largely made from the colourless transparent substances toluene, glycerol and acetone. The refractometer, by making possible rapid and accurate testing, enables the British chemical industry to maintain the highest standards in the materials it produces for the service of the community.

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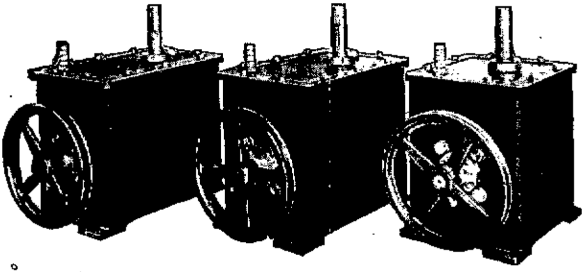

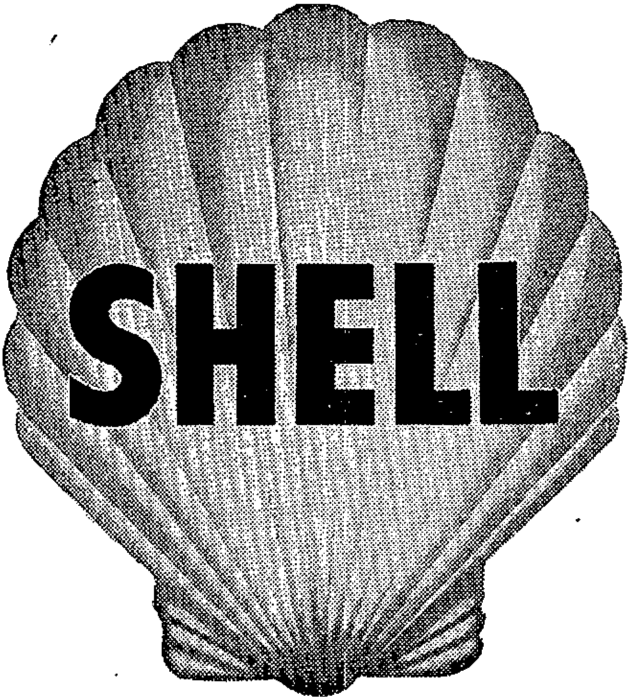
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