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Oxidation, reduction and hydrolysis of wool keratin

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NOTE TO USERS

OXIDATION, REDUCTION AND HYDROLYSIS OF WOOL KERATIN

By

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INTRODUCTION

Wool keratin, the scleroprotein of an epidermal tissue, was first classified as to its digestion by pepsin and trypsin and its insolubility in dilute acid or alkali, water or organic solvents. More recently there has been an attempt to characterize it according to the molecular ratios of histidine, lysine and arginine (1:4:12), it yields on acid hydrolysis (25).

Two percentage compositions reported for the acid hydrolysate of wool keratin are given in the table which follows:

Amino acid	Abderhalden and Voltinovici (1)	Marston (94)
Alanine	4.40	
Arginine		10.20
Aspartic acid	2.30	
Cystine	7.30	13.10
Glutamic acid	2.90	
Glycine	0.58	
Histidine		6.90
Leucine	11.50	
Lysine		2.80
Proline	4.40	
Serine	0.10	
Tryptophane		1.80
Tyrosine	2.90	4.80
Valine	2.80	

Later percentages obtained for the basic amino acids are:

Amino acid	Vickery and Block (145)	Stewart and Rimington (140)	Speakman (8)
Histidine	0.66	0.55	0.66*
Arginine	7.80	6.00	10.20*
Lysine	2.30	2.20	2.80*

*Calculated from the acid-combining capacity of wool.

Barritt has obtained 0.5 per cent of the total sulfur of wool as methionine (17), but aside from this, the whole of the sulfur has been accounted for as cystine (110). Percentages of sulfur, 1.6 to 5.4, and of nitrogen, 12.63 to 19.1, have been reported for wool (151).

There has been a tendency to ascribe all the properties of wool to its sulfur. Goddard and Michaelis have asserted that the disulfidic groups of wool are essential for maintenance of its fibrous structure even though perhaps not solely responsible for its properties (53). Harris has suggested wool is first attacked by chemical agents at the weak sulfur linkage (44) while others have attributed the stability and chemical inertness of wool to its high content of sulfur (132). The sulfur of wool has also been considered a factor in its hardness and resistance to heat but Speakman has warned against the danger of regarding the proportion of cystine as the only cause for differences among wools, among different parts of the same staple and among different cells of the same fiber (8).

The x-ray studies of animal hairs by Astbury and his associates have shown these proteins crystalline with a diffraction pattern which repeats along the direction of the axis of the fiber at a distance of 5.1 Å.U. for α-keratin, unstretched wool, and at a distance of 3.4 Å.U. for β-keratin, stretched wool (3 - 8). Astbury has pictured the wool fiber as a single chemical entity made up of bundles of chains of polypeptides

lying parallel to the axis of the fiber. He considers the polypeptides folded in α-keratin but extended to full length in β-keratin and suggests the mechanism of a reversible intramolecular transformation for the high elasticity of wool, perhaps its most valuable industrial asset.

Speakman has suggested that adjacent polypeptides are held together by lateral links which may be the disulfidic group of cystine, a salt bridge formed between diamino and dicarboxylic acids or an ether linkage from the side chains of serine, tyrosine or proline (134, 136, 137). Astbury has measured the length of the lateral links as 9.8 Å.U. (3). It has been suggested that keratin may contain one basic and one acidic side chain to every ten amino-acid residues (3) and one cystine residue to five residues of other amino acids (91).

A report of the American Association of Textile Chemists and Colorists emphasizes that "from the chemical viewpoint, wool is a very reactive substance" (44). Since wool comes in contact with many reagents during processing and use as a textile, quantitative information about its inertness or its modification by different types of reagents seems of paramount importance. This study, following that of the effect of alkali (15, 16) and hypochlorous acid (14) on wool keratin, was undertaken to obtain data of the effect of hydrochloric acid, sodium chloride, steam, sodium hydrogen sulfite and potassium permanganate on the composition and mechanical performance of wool keratin.

HISTORICAL RÉSUMÉ

Degradation of Wool Keratin by Acid

Acid is used in sterilizing, delining, carbonizing, fulling, dyeing and stripping dye from wool. Concentrated acid has been used at low temperatures as a differential solvent in the recovery of wool from mixtures (31, 38).

Treatment with dilute acid has been shown to increase the affinity of wool for acid dyes (142, 49, 113, 114) and to make the wool less resistant to alkali (114, 20-22, 74, 84) and light (114) but more resistant to moist and dry heat (48), storage (101) and weathering (65).

Dilute acids have been described as of little effect on the strength of wool below 60° C. (150, 68) and of no very destructive action below 100° C. (50, 99, 132). The isoelectric range of wool has been reported as pH 3.4 to 6.1 (40, 63, 69, 83, 97, 126, 137, 139). The rate of shrinkage of wool has been observed to increase with decrease of pH from four (131).

It has been reported that wool loses an increasing amount of nitrogen in 17.5 to 61 per cent sulfuric acid but no nitrogen in 70 percent sulfuric acid (143). Concentrated hydrochloric acid has been described as splitting hair (92) and ten normal

hydrochloric acid in five days at 20° C. as softening hair (100).

Most of the work reported has been qualitative; the quantitative work has been chiefly that of the composition of the hydrolysate rather than a study of the residual keratin.

Degradation of Wool Keratin by Neutral Salts

Sodium chloride and sodium sulfate are used as assistants in the dyebath and sodium chloride is used in a treatment of woolens to prevent shrinkage (147). Bland and Fort have reported a loss of from 0.33 to 0.50 per cent by wool on boiling with five to 20 per cent sodium sulfate for three hours (24).

Sodium chloride has been considered by Damon as the constituent of sweat detrimental to the strength of fabrics (33). In exposure to sea water and sea air (Bossolasco found 54.3 mg. chlorine per liter of air on the East African coast, (27)) wool comes in contact with chlorides. Some deterioration of a worsted fabric after 10 weeks exposure to sea water has been reported by Doree (37) and Seaber has found a much higher per cent of chloride in wool damaged by submergence in the ocean than in that unaffected (121).

A review of the literature has disclosed but few and scattered quantitative data of the effect of neutral salts on wool keratin.

Degradation of Wool Keratin by Steam

In the fabrication of wool steam is used for sterilizing, fulling (57), crabbing, decatizing, lustering, aging dyeings, producing crêpes, pressing and setting embossed designs and pile, shrinking (11), removing mill wrinkles and pressure marks (10, 148, 109), waterproofing (30, 149) and reshaping (109). Atkinson has recommended the use of steam at nine to 15 pounds (12, 13); for aging dyeings steam at 100° C. for one to three minutes has been recommended (2); steam at 10 pounds for 45 minutes has been used in finishing pile fabrics (76).

Breinl has reported that wool decomposes slowly on boiling with water at atmospheric pressure yielding volatile bases and hydrogen sulfide and, when heated with water in a sealed tube at 150° C., dissolves (28). Another investigator has found that steam at five atmospheres dissolves wool (67); Knecht once suggested the use of steam at 130° C. for removing wool from silk (79).

Polorný reported three minutes steaming unfavorable to the subsequent fixation of acid dyes by wool (104) although Fort observed that longer steaming reversed this effect resulting in a wool of increased affinity for dyes (48). Harrison has used moist heat to soften wool and render it plastic (66).

Browning of wool has been described as progressive with duration of steaming and with increase of temperature and to be

greater at 100° C. than that brought about by boiling water or dry heat (48, 70, 93, 115, 152).

Fulton and Staniford have reported that steam in 10 minutes at 12 pounds or in one hour at atmospheric pressure sterilizes blankets and uniforms without damage to the wool, which becomes friable at 60 pounds in 30 minutes (51).

Reychler has observed that wool becomes less elastic at 110° to 120° C. and decreases 12 per cent in weight and becomes friable when steamed at 135° to 150° C. (108). Sachs has reported evolution of ammonia at 130° C. and of sulfurous gases at 140° to 150° C. (115).

Hamnlein has reported the decreased elasticity but increased strength of steamed wool (62) although Scheurer has observed that wool steamed at 90° to 100° C. for 3, 6, 12, 24, 36, 48 and 60 hours loses, respectively, 18, 23, 28, 40, 50, 64, and 74 per cent of its original strength (116); Springer has confirmed Scheurer's results (139).

Increase of temperature from 100° to 180° C. has been reported by Marsh to decrease strength and weight of wool progressively (93). Although Marsh found humidity had little effect on loss of strength by wool during heating (93), Raynes has reported damage to wool caused by moist heat at 100° C. when dry heat at the same temperature did not affect the wool (105). Stirm and Rouette have noted a rapid increase in the amount of ammonia and hydrogen sulfide evolved above 100° C. and a gradual

increase in their evolution with increasing humidity (141). Elliott has described a wool fabric as losing 75 per cent of its average dry strength after 25 hours in the moist heat of an autoclave at 100° C. but only five per cent after 25 hours in the dry heat of an oven at the same temperature; at 120° C. the corresponding losses were 100 and 16 per cent (39).

Speakman has discovered that resteaming wool without tension relaxes any permanent set acquired by previous steaming under tension (133). Common examples of this are the disastrous shrinking which occurs in steam pressing a wool garment previously thinned by overstretching and the loss of wave by permanent-waved hair. Astbury and Speakman have suggested that steam first attacks the lateral linkages of keratin (8). Speakman has reported that changes in the appearance and feel of wool caused by heat are eliminated by wetting the wool in water (136).

Problems of the permanent waving of hair may lead to further study of the effect of steam on animal hairs. It would appear that disagreement among investigators as to the amount wool is damaged by heat may be traced to the few, and those qualitative, data available.

Degradation of Wool Keratin by Reducing Agents

The oldest known method of bleaching wool is the sulfur dioxide method in which wool may be exposed to the gas for six

to 24 hours (95) or immersed in its aqueous solution or one of sodium hydrogen sulfite. Matthews has recommended bleaching wool for six to 10 hours with 1.7 per cent solution of sodium hydrogen sulfite followed by treatment with one per cent sulfuric acid (95); the use of 15 per cent sodium hydrogen sulfite for 10 to 15 hours has been recommended for bleaching (71, 72, 46) and as an addition to the carbonizing bath (79). The adsorption of sulfur dioxide by wool has been described (102, 106, 107); Reychler has reported a maximum adsorption of 0.38 mole of sulfur dioxide per kilogram of wool (107).

Sodium hydrogen sulfite has also been recommended for mercerization (41), production of crêpes (76) and for increasing the luster (42) and affinity of wool for dyes (42, 43). Polorny has reported treatment with sodium hydrogen sulfite as unfavorable to the fixation of acid dyes on wool although increasing the affinity of wool for basic dyes (104); König has reported similar results with sodium thiosulfate (82).

While treatment with solutions of sodium hydrogen sulfite has been found by Udalm (144) and Rinoldi (112) to decrease the strength of wool, Sirocco and Khelemskiĭ have used it to protect hair from hydrolytic degradation during the unhairing of hides (125). Croeder and Harris have described sodium sulfide as protecting the sulfur in wool from the action of alkali (32). It has also been noted that sodium hydrosulfite (60) and stannous chloride (103) weaken wool, and lithium hydrogen sulfide, thioglycolic acid, sodium sulfide and potassium cyanide have been

shown to render keratin digestible by pepsin or trypsin (53, 87).

Goddard and Michaelis (53) have reported the following percentages for derivatives prepared from wool keratin by reductants:

	Wool	Protein A	Protein B	Protein C
Nitrogen	16.66	15.71	15.99	12.99
Sulfur	3.19	3.20	1.80	6.60

Protein A was prepared by treatment for 24 hours with sodium thioglycolate; protein B by treatment for 24 hours with potassium cyanide; protein C by treatment for 48 hours with sodium sulfide. Lithium hydrogen sulfide, thioglycolic acid, sodium sulfide and potassium cyanide have been found to react with keratin only in alkaline solutions (53, 87, 132) and Goddard and Michaelis have suggested destruction of salt linkages may necessarily precede attack of disulfidic lateral linkages by reductants (53).

Although sulfur bleaches have been widely used for wool there has been scarcely any study of their effect on the integrity of keratin, two investigators, Udaka and Rinoldi, have noted loss of strength by wool when treated with sodium hydrogen sulfite but have presented no analytical data as evidence.

Degradation of Wool Keratin by Oxidizing Agents

Oxidizing agents such as ozone, halogens, hypohalogen acids, potassium permanganate, potassium dichromate, hydrogen peroxide, sodium peroxide, perborates, persulfates, and per-

carbonates have been used for sterilizing (35, 36), carbonizing, carroting (19), bleaching, producing unshrinkable finishes (14), mordanting (124), dyeing (85), printing (90) and desulfurizing (123) wool.

A number of different concentrations of potassium permanganate have been recommended; 0.4 per cent solution has been suggested for bleaching feathers and hair (57); 0.1 per cent solution has been recommended for bleaching animal fibers (55); Matthews has suggested bleaching wool with potassium permanganate, one to four per cent of the weight of wool (95); and Rinoldi has specified 20 volumes of 0.3 per cent potassium permanganate for bleaching wool (111).

Wool bleached with hydrogen peroxide has been described as harsh (129) and that bleached in a solution of potassium permanganate, containing the amount of acid theoretically required to prevent formation of manganese dioxide, has been reported of decreased felting power and increased affinity for dyestuffs (78).

Folgner and Schneider have stated that damaged wool is more rapidly attacked by hydrogen peroxide than undamaged wool (47) and treatment with three per cent hydrogen peroxide for 24 hours at room temperature has been found to make wool more susceptible to alkaline solutions (85, 130). Smith and Harris have reported no significant changes in wet strength or total sulfur and a lower content of cystine and higher solubility

in alkali for conditioned wool yarn oxidized by hydrogen peroxide than for untreated wool (127); wool chlorinated by 0.06 N hypochlorous acid in one hour at 25° C. has been found more susceptible to acid as well as to alkali (14). It has been noted that wool bleached with hydrogen peroxide gives no reaction with lead sulfide (23, 128).

Gardner and Carter have reported 1.65 per cent loss in weight for wool boiled two hours with potassium dichromate (52) and Liechti and Hummel have described the evolution of ammonia upon boiling wool with potassium dichromate (36).

Treatment of wool for one hour at 50° C. with a solution of two-volume hydrogen peroxide at pH 9.5 has been reported to change 2.2 per cent of the sulfur in the residual wool to sulfate (128); bromine water has been reported to convert 7.2 per cent of the sulfur of wool to sulfate (26). Boiling 30 per cent hydrogen peroxide (29), nitric acid (26), and boiling potassium dichromate (120) have been described as converting all the sulfur of wool to sulfate. Haller and Munk have found that treatment of wool in 30 per cent hydrogen peroxide at room temperature changes the sulfur to sulfuric or persulfuric acid (61). Liesizin has described digestion in two per cent potassium permanganate as converting nine per cent of the sulfur of hair to sulfuric acid, 2.5 per cent to a compound named by him oxykeratin-sulfonic acid, and 88.5 per cent to cysteic acid (88, 89). Oxidation by potassium permanganate of a solution

of wool in potassium hydroxide was early reported by Wanklyn and Cooper as yielding carbonic acid, oxalic acid, and cyanopropionic acid (146). Schöberl has noted that the oxidation velocity for organic compounds of sulfur shows specific dependence on the concentration of alkali (118). It has been suggested that the oxidation of keratin proceeds differently than that of cystine.

Most of the available quantitative data deal with the effect of oxidizing agents on keratin which has been brought into solution by acid or alkali.

EXPERIMENTAL PROCEDURE

Materials

1. Wool keratin. The keratin was prepared from plain-woven undyed wool batiste which was boiled for one hour in one hundred times its weight of distilled water, dried, cut for analysis and extracted continuously with ether for eighteen hours in a modified Soxhlet extractor. The Cotswold wool fiber was previously purified in this laboratory (151). The analysis of these wools for ash, sulfate sulfur and sulfite sulfur is given in table A.

2. Ammonium nitrate. C.P. General Chemical Co.

3. Barium chloride. C.P. General Chemical Co.

4. Benedict-Denis Reagent. Twenty-five grams of copper nitrate ($Cu(NO_3)_2 3H_2O$, 25 grams of sodium chloride, and 10 grams of ammonium nitrate were made up to 100 cc. with water (34).

5. Cupric nitrate. C.P. General Chemical Co.

6. Ether. Anhydrous, sp. gr. 0.72. J.T. Baker and Co.

7. Hydrochloric acid. C.P., sp. gr. 1.18-1.19. General Chemical Co.

   a. A solution for reference was standardized by precipitating the chlorine as silver chloride which was weighed. All concentrations of alkali and

Table A.

Ash, sulfate sulfur and sulfite sulfur of wool fiber.

Keratin	Sample	Ash		Barium sulfate	Sulfate sulfur	Sulfite sulfur
	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin
Fabric I.	1.1236			0	0	
	1.3251			0	0	
Average					0	
Average deviation					0	
Fabric II.	5.5503	0.0150	0.27			
	5.5053	0.0186	0.33			
	5.7002			0	0	
	5.2335			0	0	
	5.4318			0.0778		0.20
	5.3530			0.0783		0.20
Average			0.30		0	0.20
Average deviation			0.03		0	0.0
Fabric III.	4.4737	0.0000	0.00			
	4.3518	0.0006	0.01			
	4.3116			0.2394	0.92	
	4.3710			0.2964	0.93	
	4.9196			0.0734		0.20
	4.8946			0.0722		0.20
Average			0.01		0.93	0.20
Average deviation			0.01		0.01	0.00
Cotswold wool fiber	2.4663			0.0447		0.25
	2.6012			0.0450		0.24
Average						0.25
Average deviation						0.01

acid refer to this standard.

b. The dilute solutions of hydrochloric acid were standardized by titration against a standard solution of sodium hydroxide using Methyl Red as an indicator.

c. The concentrated solutions of hydrochloric acid were made by diluting C.P. acid with distilled water to sp. gr. 1.112 or 1.126 and were standardized by converting the chlorine into silver chloride which was weighed.

8. Iodine. Resublimed. Merck. A tenth molal solution was prepared by dissolving 127 grams of iodine in one liter of 10 per cent potassium iodide solution.

9. Mercury. C.P. J.T. Baker and Co.

10. Nitric acid. C.P., sp. gr. 1.42. General Chemical Co.

11. Paraffin. Standard Oil Co.

12. Potassium chromate. General Chemical Co.

13. Potassium hydroxide. C.P. General Chemical Co.

14. Potassium iodide. C.P. General Chemical Co.

15. Potassium permanganate. C.P. General Chemical Co.

Solutions were prepared by dissolving the C.P. reagent in boiled distilled water, allowing them to stand for several days in a tightly stoppered brown bottle and then filtering them through acid-digested asbestos to remove any precipitated manganese dioxide. The solutions were standardized against sodium oxalate

in a hot solution of sulfuric acid (44).

16. Potassium sulfide. C.P. J.T. Baker and Co.

17. Silver nitrate. Reagent. Merck and Co. 0.2 N Silver nitrate was standardized by titrating a standard hydrochloric acid solution, using potassium chromate as an indicator (45).

18. Sodium chloride. C.P. General Chemical Co. The calculated amount of C.P. reagent was dissolved in chloride-free distilled water and standardized by the Mohr method (45), titration in neutral solution with fifth normal silver nitrate using potassium chromate as an indicator.

19. Sodium hydrogen sulfite. C.P. General Chemical Co.

a. The calculated amount of C.P. reagent was dissolved in distilled water and standardized by titration of the iodine liberated from an acidified solution of potassium iodide by 25 cc. of 0.1000 N potassium permanganate (119).

b. A 0.5 per cent solution was prepared by dissolving C.P. reagent in distilled water.

20. Sodium hydroxide. C.P. General Chemical Co. A dilute solution was standardized by titration with standard hydrochloric acid using Methyl Red as an indicator.

21. Sodium oxalate. C.P. General Chemical Co.

22. Sodium sulfate. C.P. General Chemical Co.

23. Stannous chloride. C.P. General Chemical Co. One hundred grams were dissolved in 100 cc. of nearly boiling con-

centrated hydrochloric acid and diluted with 50 cc. of water.

24. Sulfuric acid. C.P., sp. gr. 1.84. General Chemical Co.

25. Zinc. Mossy. Wilkins-Anderson.Co.

Methods of Analysis

Degradation of wool keratin by hydrochloric acid and sodium chloride.

A sample of wool keratin I, dried to constant weight in an electric oven at 105° C., (method of tares was used in all weighings) was immersed in 125 cc. of water or hydrochloric acid in a stoppered flask maintained at 25° ± 0.1° C. in a water bath for 10 hours and then washed with distilled water until the rinse gave no test for chloride.

For the tests at 100° C., a sample of keratin II was placed in 250 cc. of water, hydrochloric acid or sodium chloride in a 500 cc. flask fitted with a water-cooled reflux condenser and heated in a boiling water bath for one hour. Titration of blank determinations showed no concentration of the solution during boiling.

Ten weighed samples and 10 breaking strength strips were treated at each concentration. The strips for test of strength were broken wet immediately after rinsing; the elongation was read from an autographic recorder. The weighed samples were

air-dried, five were analyzed for nitrogen and five were again brought to constant weight before analysis for sulfur.

Degradation of wool keratin by steam.

Keratin II was steamed for one hour at 100°, 115.2°, 121°, 126°, 134.5°, or 141.5° C. and for one, three or five hours at 115.2° C. in an autoclave equipped with an accurate pressure gauge and thermometer. The samples were hung on glass rods placed across Pyrex beakers and protected from condensed liquid by an inverted watch glass so that no metal and no liquid which had flowed across metal came in contact with the keratin. Soluble products of its degradation were washed from the fabric by eight rinsings in distilled water before analysis of the residual keratin.

Degradation of wool keratin by sodium hydrogen sulfite.

A sample of wool keratin III was immersed in 50 volumes of 0.9525 M sodium hydrogen sulfite in a stoppered flask maintained at 40° ± 0.1° C. in a water bath for 10 hours, and before analysis washed until the rinse no longer decolorized permanganate.

Degradation of wool keratin by potassium permanganate.

A sample of wool keratin III was immersed in 50 volumes

of 0.01 to 0.04 M potassium permanganate or 0.01 to 0.06 M potassium permanganate made 0.18 N with sulfuric acid, in 62.5, 75, 87.5 or 100 volumes of 0.02 M potassium permanganate or 0.02 M acidified potassium permanganate in a stoppered flask maintained at 40° ± 0.1° C. in a water bath for 10 hours. The residues were freed from oxides of manganese by 0.5 per cent solution of sodium hydrogen sulfite in two hours at room temperature, washed in distilled water until the rinse no longer decolorized permanganate and then analyzed.

Determination of ash.

A sample which had been brought to constant weight was ignited to constant weight in a muffle furnace at dull red heat.

Determination of breaking strength and elongation at breaking load.

A Scott universal tester with autographic recorder was used to determine the wet warp strength and elongation at breaking load by the one-inch strip method (9). The two-inch jaws of the machine were clamped three inches apart on the strip and the machine was run at the rate of 12 inches per minute until the fabric was strained to its breaking point.

Determination of total nitrogen.

The keratin was converted into colorless solution by 50 cc. of boiling concentrated sulfuric acid containing a drop of mercury and 10 grams of sodium sulfate. After cooling and diluting the solution with 200 cc. of water, a small piece of paraffin, 160 cc. of 40 per cent sodium hydroxide, 20 cc. of 10 per cent potassium sulfide and a few small pieces of zinc were added and the mixture was distilled at once into a measured volume of standard hydrochloric acid. The excess of acid was titrated with standard sodium hydroxide using Methyl Red as an indicator.

Determination of sulfur.

Total sulfur. The keratin was dissolved by digestion with 100 cc. of a solution one part concentrated nitric acid, two parts water. After the addition of 100 cc. of Benedict-Denis reagent (34) the solution was evaporated to dryness, the residue heated to dull redness for 10 minutes, dissolved in 100 cc. of 10 per cent hydrochloric acid and filtered. The filtrate was heated to boiling and the sulfur precipitated as barium sulfate by the addition of 25 cc. of 10 per cent barium chloride. After 12 to 15 hours the precipitate was filtered into a weighed Gooch crucible, washed free of chloride and ignited to constant weight at dull red heat in a muffle furnace. Blank determinations were

made to determine the sulfur of the reagents.

Sulfate sulfur. Five grams of wool were dissolved by heating in a water bath with 50 cc. of 30 per cent hydrochloric acid. The solution was cooled, diluted with an equal volume of water and filtered. The filtrate was brought to boiling and its sulfur precipitated as barium sulfate by the addition of 25 cc. of 10 per cent barium chloride. The precipitate was filtered, washed free of chloride and ignited to constant weight (96).

Sulfite sulfur. Five grams of wool were placed with 60 cc. of a solution of stannous chloride and 10 cc. of 10 per cent barium chloride in a balloon flask fitted with a delivery tube dipping into a flask containing 100 cc. of 10 percent potassium hydroxide and 50 to 100 cc. of 0.1 N iodine solution. After the contents of the balloon flask were boiled vigorously for 30 minutes, the alkaline iodine solution was boiled for a few minutes, filtered, acidified with hydrochloric acid, concentrated to a small volume and again filtered. This filtrate was heated to boiling before precipitation of the sulfur as barium sulfate with 10 per cent barium chloride. The precipitate was filtered, washed free of chloride and ignited to constant weight. The amount of sulfur was compared with that obtained by treating a sample of Cotswold wool in the same manner (54).

Table I

Effect of hydrochloric acid in ten hours at 25° C. on the weight, total sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin

Determination	Hydrochloric acid	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
1	0	6.4650	6.4442	99.7	1.8587	3.95			
2		6.4913	6.4774	99.8	1.8461	3.91			
3		6.4739	6.4600	99.8	1.8526	3.93			
4		6.4903	6.4871	99.9	1.8593	3.93			
5		6.4871	6.4778	99.9	1.8604	3.94			
Average				99.8		3.93	3.94	19	68
Average deviation				0.1		0.01		0.8	3
1	0.1000	6.4370	6.4366	100.0	1.8380	3.92			
2		6.4403	6.4426	100.0	1.8353	3.91			
3		6.7000	6.6768	99.6	1.9335	3.96			
4		6.3002	6.2908	99.8	1.7921	3.91			
5		6.4394	6.4314	99.9	1.8624	3.97			
Average				99.9		3.93	3.93	19	68
Average deviation				0.1		0.02		0.8	2
1	0.2500	6.5543	6.5173	99.4	1.8697	3.92			
2		6.3041	6.2931	99.9	1.8131	3.95			
3		6.3368	6.3257	99.8	1.8444	3.97			

Table I. Continued.

Determination	Hydrochloric acid	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
Average				99.7		3.95	3.96	19	68
Average deviation				0.2		0.02		0.7	2
1	0.5000	6.6589	6.6284	99.5	1.8744	3.87			
2		6.3723	6.3400	99.5	1.7856	3.85			
3		6.4560	6.4268	99.5	1.8281	3.89			
Average				99.5		3.87	3.89	19	69
Average deviation				0.0		0.01		0.6	2
1	1.0000	6.4246	6.4166	99.9	1.8098	3.87			
2		6.4231	6.4134	99.8	1.7765	3.80			
3		6.6604	6.6670	100.0	1.8594	3.83			
Average				99.9		3.83	3.83	18	65
Average deviation				0.1		0.02		1.5	3
1	6.8645	6.5775	6.1633	93.7	1.8313	3.82			
2		6.5275	6.1727	94.6	1.8034	3.79			
3		6.2422	5.8967	94.5	1.7333	3.81			
Average				94.3		3.81	4.04	10	65
Average deviation				0.4		0.01		0.7	3
1	7.8690	6.5124	5.7971	89.0	1.7901	3.78			
2		6.5724	5.8312	88.7	1.7976	3.76			
3		6.6580	5.9014	88.6	1.8009	3.72			
Average				88.8		3.75	4.22	<1	--
Average deviation				0.2		0.02		--	--

Table II

Effect of hydrochloric acid in ten hours at 25° C. on the total nitrogen of wool keratin.

Determination	Hydrochloric acid molality	Keratin gram	Hydrochloric acid molality	Hydrochloric acid cc.	Sodium hydroxide cc. 0.2260 M	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	0	6.4575	0.2585	300.00	4.90	16.58	
2		6.7725		312.30	1.68	16.62	
3		6.6762		310.90	5.00	16.63	
4		6.7242		306.50	1.40	16.55	
Average						16.60	16.63
Average deviation						0.03	
1	0.1000	6.7670	0.2070	400.10	11.90	16.58	
2		6.6875		400.00	16.30	16.57	
Average						16.58	16.60
Average deviation						0.01	
1	0.2500	6.5615	0.2585	300.00	1.30	16.49	
2		6.4406		300.30	6.45	16.57	
Average						16.53	16.58
Average deviation						0.04	
1	0.5000	6.4770	0.2585	300.30	7.40	16.43	
2		6.4934		300.00	5.20	16.48	
3		6.3096		300.00	15.20	16.45	
Average						16.45	16.53
Average deviation						0.02	

Table II. Continued.

Determination	Hydrochloric acid molality	Keratin gram	Hydrochloric acid molality	Hydrochloric acid cc.	Sodium hydroxide cc. 0.2260 N	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	1.0000	6.4933	0.2070	400.00	26.10	16.57	
2		6.5960			22.40	16.50	
Average						16.54	16.56
Average deviation						0.04	
1	6.8645	6.7131	0.2535	300.00	13.00	15.57	
2		6.4968			23.00	15.60	
3		6.5726			18.65	15.63	
Average						15.60	16.54
Average deviation						0.02	
1	7.8690	6.6483	0.2535	300.00	37.70	14.54	
2		6.5997			41.60	14.47	
3		6.5684			43.30	14.45	
4		6.4171		300.20	50.00	14.47	
Average						14.48	16.31
Average deviation						0.03	

Table III

Effect of hydrochloric acid in one hour at 100° C. on the weight, total sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin

Determination	Hydrochloric acid	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
1	0	6.1103	6.0681	99.3	1.6564	3.72			
2		6.3014	6.2598	99.3	1.7714	3.86			
3		5.9810	5.9360	99.2	1.6504	3.79			
Average				99.3		3.79	3.82	14	62
Average deviation				0.1		0.05		0.9	3
1	0.2500	6.1291	5.8930	96.1	1.6643	3.73			
2		5.9583	5.7073	95.8	1.6656	3.84			
3		5.8381	5.6193	96.2	1.6201	3.81			
Average				96.0		3.79	3.95	8	62
Average deviation				0.2		0.04		0.2	2
1	0.5000	5.6410	5.1560	91.4	1.5284	3.72			
2		5.9150	5.4608	92.3	1.5982	3.71			
3		6.0309	5.5480	92.0	1.6306	3.71			
Average				91.9		3.71	4.04	2	59
Average deviation									

Table III. Continued.

Determination	Hydrochloric acid	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
1	0.7500	5.4221	4.6297	85.4	1.4641	3.71			
2		5.9164	5.0077	84.6	1.6063	3.73			
3		5.4195	4.6361	85.5	1.4514	3.68			
Average				85.2		3.71	4.35	<1	--
Average deviation				0.4		0.02		--	--

Table IV

Effect of hydrochloric acid in one hour at 100° C. on the total nitrogen of wool keratin.

Determination	Hydrochloric acid molality	Keratin gram	Hydrochloric acid cc. 0.1945 M	Sodium hydroxide cc. 0.2160 M	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	0	5.8203	400.00	42.00	16.54	
2		5.7525		44.32	16.61	
3		6.1442	405.00	27.70	16.59	
Average					16.58	16.70
Average deviation					0.03	
1	0.2500	6.0782	400.00	43.20	15.73	
2		5.7614		60.00	15.76	
3		5.7376		60.80	15.79	
Average					15.76	16.44
Average deviation					0.01	
1	0.5000	5.4776	408.10	100.00	14.76	
2		5.6327	414.00	100.00	14.66	
3		5.1322	400.00	109.20	14.63	
Average					14.69	15.98
Average deviation					0.06	
1	0.7500	5.4772	400.00	114.50	13.57	
2		6.0323	409.35	100.00	13.47	
3		5.7960	400.85	103.00	13.47	
4		6.0260	410.82	100.00	13.55	
Average					13.52	15.87
Average deviation					0.05	

Table V

Effect of sodium chloride in one hour at 100° C. on the weight, total sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin

Determination	Sodium chloride	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
1	0.0604	5.5576	5.5051	99.1	1.5477	3.82			
2		5.7256	5.6767	99.1	1.5770	3.76			
3		5.5029	5.4339	98.7	1.5515	3.87			
Average				99.0		3.82	3.86	16	54
Average deviation				0.2		0.03		0.5	3
1	0.7049	5.4742	5.4221	99.0	1.5139	3.80			
2		5.3964	5.3503	99.1	1.4775	3.76			
3		5.4101	5.3544	99.0	1.4900	3.76			
Average				99.0		3.78	3.82	15	57
Average deviation				0.1		0.01		0.7	4

Table VI

Effect of sodium chloride in one hour at 100° C. on the total nitrogen of wool keratin.

Determination	Sodium chloride: molality	Keratin: gram	Hydrochloric acid: molality	Hydrochloric acid: cc.	Sodium hydroxide: cc. 0.2160 M	Nitrogen: percentage of keratin	Nitrogen: percentage of residue
1	0.0604	5.9922	0.1945	400.25	38.80	16.24	
2		5.4867	0.3150	226.00	34.40	16.28	
3		5.4482		225.00	36.60	16.19	
Average						16.24	16.40
Average deviation						0.03	
1	0.7049	5.4719	0.1945	400.00	60.95	16.55	
2		5.4435			65.00	16.41	
3		5.2805			72.85	16.46	
Average						16.47	16.64
Average deviation						0.05	

Table VII

Effect of steam in one hour on the weight, total sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin

Determination	Temperature	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
	°C.	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	100.0	5.5136	5.4719	99.2	1.5647	3.90			
2		5.5406	5.5058	99.4	1.5734	3.90			
3		5.9647	5.9413	99.6	1.6666	3.84			
4		5.5692	5.5257	99.2	1.5681	3.87			
Average				99.4		3.88	3.90	13	50
Average deviation				0.2		0.02		0.6	3
1	115.2	5.9094	5.8618	99.2	1.5912	3.70			
2		5.7763	5.7147	98.9	1.5717	3.74			
3		5.6992	5.6390	98.9	1.5627	3.77			
Average				99.0		3.74	3.78	11	55
Average deviation				0.1		0.02		0.8	6
1	121.0	5.4217	5.3943	99.5	1.4844	3.76			
2		5.8778	5.8124	98.9	1.5988	3.74			
3		5.7641	5.7276	99.0	1.5779	3.75			
Average				99.1		3.75	3.78	8	40
Average deviation				0.2		0.01		1.0	2
1	126.0	5.5698	5.5246	98.8	1.5404	3.78			
2		5.8589	5.7981	99.0	1.5923	3.73			
3		5.8979	5.8192	98.7	1.6103	3.75			

Table VII. Continued.

Determination	Temperature °C.	Keratin: gram	Residue: gram	Residue: percentage of keratin	Barium sulfate: gram	Total sulfur: percentage of keratin	Total sulfur: percentage of residue	Breaking strength of wet warp: pounds per inch	Elongation at breaking load: percentage
4		5.6674	5.6126	99.0	1.5460	3.75			
Average				98.9		3.75	3.79	2	49
Average deviation				0.1		0.01		1.3	2
1	134.6	5.4928	5.4232	98.7	1.4774	3.69			
2		5.7742	5.6936	98.6	1.5349	3.65			
3		5.9361	5.7827	98.7	1.5576	3.65			
Average				98.7		3.68	3.73	<1	--
Average deviation				0.1		0.02		--	--
1	141.6	5.0837	4.7450	93.3	1.2113	3.29			
2		5.3044	4.9091	92.6	1.2899	3.34			
3		5.0478	4.8398	95.9	1.2308	3.37			
Average				93.9		3.33	3.55	<1	--
Average deviation				1.3		0.03		--	--

Table VIII

Effect of steam in one hour on the total nitrogen of wool keratin.

Determination	Temperature °C.	Keratin gram	Hydrochloric acid cc. 0.3150 N	Sodium hydroxide cc. 0.2160 N	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	100.0	5.3573	225.00	35.70	16.52	
2		5.6472		21.05	16.45	
3		5.4574		33.30	16.35	
Average					16.44	16.54
Average deviation					0.06	
1	115.2	5.6102	225.00	23.75	16.42	
2		5.4504		32.90	16.39	
3		5.5466		25.70	16.50	
Average					16.44	16.61
Average deviation					0.04	
1	121.0	5.5328	225.00	30.80	16.26	
2		5.6493		24.65	16.25	
3		5.4451		35.70	16.25	
Average					16.25	16.40
Average deviation					0.01	
1	126.0	6.0510	250.00	36.10	16.43	
2		5.8878	225.20	9.50	16.39	
3		5.8586	225.00	13.50	16.25	
Average					16.36	16.54
Average deviation					0.06	

Table VIII. Continued.

Determination	Temperature °C.	Keratin gram	Hydrochloric acid cc. 0.3150 N	Sodium hydroxide cc. 0.2160 N	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	134.5	5.5062	225.1	35.45	16.09	
2		5.8902	225.0	13.15	16.18	
3		5.4711		36.85	16.11	
Average					16.13	16.34
Average deviation					0.04	
1	141.5	5.1701	225.00	60.35	15.67	
2		5.1493		59.75	15.77	
3		5.1853		57.90	15.77	
4		5.2764		55.10	15.66	
Average					15.72	16.74
Average deviation					0.05	

Table IX

Effect of steam at 115.2° C. on the weight, total sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin.

Determination	Time	Keratin	Residue		Barium sulfate	Total sulfur		Breaking strength of wet warp	Elongation at breaking load
			gram	percentage of keratin	gram	percentage of keratin	percentage of residue	pounds per inch	percentage
	hour								
1	3	5.6709	5.6183	99.1	1.5675	3.90			
2		5.5782	5.5289	99.1	1.5114	3.72			
3		5.8181	5.7681	99.1	1.5906	3.78			
Average				99.1		3.76	3.79	7	42
Average deviation				0.0		0.03		1.1	4
1	5	5.2160	5.1285	98.3	1.4073	3.71			
2		5.7977	5.7300	98.8	1.5470	3.66			
3		5.7604	5.6934	98.8	1.5499	3.69			
Average				98.6		3.69	3.74	2	47
Average deviation				0.2		0.02		0.8	1

Table X

Effect of steam at 116.2° C. on the total nitrogen of wool keratin.

Determination	Time	Keratin	Sodium hydroxide*	Nitrogen	
	hour	gram	cc. 0.2160 M	percentage of keratin	percentage of residue
1	3	5.7816	15.60	16.36	
2		5.5494	27.00	16.42	
Average				16.39	16.54
Average deviation				0.03	
1	5	5.8376	22.05	15.86	
2		5.6157	33.70	15.86	
3		5.6352	36.15	15.68	
Average				15.80	16.02
Average deviation				0.08	

*The ammonia was distilled into 225.00 cc. 0.3150 M hydrochloric acid.

Table XI

Effect of fifty volumes of 0.9525 M sodium hydrogen sulfite in ten hours at 40° C. on the weight, sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin.

Determination	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	3.9912	3.9534	99.0	1.3659	4.70			
2	3.9328	3.8975	99.1	1.3572	4.74			
3	3.7079	3.6649	98.8	1.2735	4.72			
4	4.4393			0.2306		0.87		
5	3.9652			0.2433		0.84		
Average			99.0		4.72	0.86	5	60
Average deviation			0.1		0.01	0.01	1.0	3

Table XII

Effect of fifty volumes of 0.9525 M sodium hydrogen sulfite in ten hours at 40° C. on the total nitrogen of wool keratin.

Determination	Keratin	Sodium hydroxide*	Nitrogen	
	gram	cc. 0.2396 M	percentage of keratin	percentage of residue
1	3.7605	24.80	16.26	
2	3.8080	22.30	16.28	
3	3.9035	17.70	16.26	
Average			16.26	16.42
Average deviation			0.01	

*The ammonia was distilled into 150.00 cc. 0.3305 N hydrochloric acid.

Table XIII

Effect of fifty volumes of aqueous potassium permanganate in ten hours at 40° C. on the weight, sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	0	4.4076	4.3602	98.9	1.4998	4.67			
2		4.3972	4.3426	98.8	1.4991	4.68			
3		4.3181	4.2791	99.1	1.4727	4.68			
4		4.3116			0.2894		0.92		
5		4.3710			0.2964		0.93		
Average				98.9		4.68	0.93	10	50
Average deviation				0.1		0.01	0.01	0.3	3
1	0.0100	4.4517	4.2922	96.4	1.4724	4.54			
2		4.3122	4.1795	96.9	1.4248	4.54			
3		4.1994			0.2799		0.92		
4		4.2670			0.2815		0.91		
Average				96.7		4.54	0.92	7	47
Average deviation				0.3		0.00	0.01	0.8	3
Average	0.0150							4	40
Average deviation								1.0	3
1	0.0200	4.4267	4.1048	92.7	1.4033	4.36			
2		4.3220	3.9805	92.1	1.3778	4.38			
3		3.9260	3.6309	92.5	1.2663	4.40			

Table XIII. Continued.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of Keratin	gram	percentage of Keratin	percentage of Keratin	pounds per inch	percentage
4		4.3304	3.9858	92.0	1.3584	4.31			
5		3.7763			0.2049		0.82		
6		3.8867			0.2123		0.79		
Average				92.3		4.36	0.81	3	33
Average deviation				0.3		0.03	0.02	0.9	3
1	0.0300	4.4782	3.7097	82.8	1.4011	4.30			
2		3.9125	3.3604	85.9	1.2070	4.24			
3		4.2480	3.5100	82.6	1.3087	4.23			
4		3.9093			0.2608		0.92		
5		3.9050			0.2505		0.88		
Average				83.8		4.26	0.90	<1	--
Average deviation				1.4		0.03	0.02	--	--
1	0.0400	4.5177	3.4362	76.1	1.2768	3.88			
2		4.2610	3.2268	75.6	1.1829	3.81			
3		4.3450	3.3560	77.2	1.2303	3.84			
4		3.7406			0.2468		0.91		
5		3.7302			0.2446		0.88		
Average				76.3		3.84	0.90	<1	--
Average deviation				0.6		0.02	0.02	--	--

Table XIV

Effect of fifty volumes of aqueous potassium permanganate in ten hours at 40° C. on the total nitrogen of wool keratin.

Determination	Potassium permanganate molality	Keratin gram	Hydrochloric acid molality	Hydrochloric acid cc.	Sodium hydroxide molality	Sodium hydroxide cc.	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	0	4.5110	0.3150	200.00	0.2370	46.70	16.13	
2		4.2700	0.3305	150.00	0.2387	2.20	16.06	
3		4.3115		175.00		34.30	16.13	
Average							16.11	16.29
Average deviation							0.03	
1	0.01	4.3182	0.3150	200.00	0.2370	60.90	15.76	
2		4.6041	0.3305	175.00	0.2387	26.90	15.64	
3		4.4471				33.70	15.69	
Average							15.70	16.24
Average deviation							0.04	
1	0.02	4.3948	0.3305	200.00	0.2387	68.50	14.91	
2		4.4038				68.10	14.91	
3		4.3622				68.00	14.99	
Average							14.94	16.19
Average deviation							0.04	
1	0.03	4.4408	0.3305	150.00	0.2387	12.50	13.97	
2		4.3680				16.50	13.90	
3		4.6336				4.40	13.97	
4		4.4943				9.90	14.00	
Average							13.96	16.34
Average deviation							0.03	

Table XIV. Continued.

Determination	Potassium permanganate molality	Keratin gram	Hydrochloric acid molality	Hydrochloric acid cc.	Sodium hydroxide molality	Sodium hydroxide cc.	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	0.04	4.4079	0.3305	150.00	0.2387	37.70	12.90	
2		4.3164				41.50	12.87	
3		4.2624		150.10		44.20	12.84	
Average							12.87	16.87
Average deviation							0.02	

Table XV

Effect of 0.02 N aqueous potassium permanganate in ten hours at 40° C. on the weight and sulfur of wool keratin.

Determination	Potassium permanganate: cc. per gram keratin	Keratin: gram	Residue: gram	Residue: percentage of keratin	Barium sulfate: gram	Total sulfur: percentage of keratin	Sulfate sulfur: percentage of keratin
1	62.50	4.3974	3.9148	89.0	1.3649	4.26	
2		4.4939	3.9907	88.5	1.4170	4.33	
3		4.4501	3.9290	88.1	1.3997	4.31	
4		4.0766			0.2757		0.94
5		4.0456			0.2547		0.86
Average				88.5		4.30	0.90
Average deviation				0.3		0.03	0.04
1	75.00	4.3519	3.6703	84.3	1.2585	3.97	
2		4.4436	3.7546	84.5	1.3103	4.05	
3		4.2608	3.7893	88.9	1.2325	3.97	
4		3.3690			0.2211		0.90
5		4.1654			0.2623		0.83
Average				85.9		4.00	0.87
Average deviation				2.0		0.04	0.04
1	87.50	4.6278	3.6114	78.0	1.2757	3.86	
2		5.0116	4.0673	81.2	1.4325	3.93	
3		4.6305			0.3302		1.00
4		4.5145			0.3153		0.96
Average				80.5		3.90	0.98
Average deviation				0.7		0.04	0.02

Table XV. Continued.

Determination	Potassium permanganate: cc. per gram keratin	Keratin: gram	Residue: gram	Residue: percentage of keratin	Barium sulfate: gram	Total sulfur: percentage of keratin	Sulfate sulfur: percentage of keratin
1	100.00	4.3071	3.3291	75.9	1.2350	3.87	
2		4.3982	3.2979	74.9	1.2177	3.81	
3		3.9803	2.9378	75.7	1.0678	3.73	
4		4.5082			0.3823		0.96
5		4.5716			0.3068		0.92
Average				75.5		3.82	0.94
Average deviation				0.4		0.03	0.02

Table XVI

Effect of 0.02 M aqueous potassium permanganate in ten hours at 40° C. on the total nitrogen of wool keratin.

Determination	Potassium permanganate: cc. per gram keratin	Keratin: gram	Sodium hydroxide* : cc. 0.2386 M	Nitrogen: percentage of keratin	Nitrogen: percentage of residue
1	62.50	4.4847	14.40	14.41	
2		4.4216	16.70	14.44	
3		4.3108	21.55	14.44	
Average				14.43	16.31
Average deviation				0.01	
1	75.00	4.4210	22.30	14.02	
2		4.4250	22.40	14.00	
3		4.4268	23.45	13.94	
Average				13.99	16.29
Average deviation				0.03	
1	87.50	4.4425	28.90	13.46	
2		4.4654	28.60	13.41	
3		4.4844	27.00	13.47	
Average				13.44	16.70
Average deviation				0.03	
1	100.00	4.4743	36.10	12.82	
2		4.4681	34.10	12.99	
3		3.9050	58.00	12.82	
Average				12.88	17.07
Average deviation				0.08	

*The ammonia was distilled into 150.00 cc. 0.3306 M hydrochloric acid.

Table XVII

Effect of fifty volumes of acidic potassium permanganate in ten hours at 40° C. on the weight, sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	0.0100	4.4254	4.2806	96.7	1.5000	4.66			
2		4.5147	4.3668	96.7	1.5419	4.69			
3		4.5431	4.3976	96.8	1.5512	4.69			
4		3.8830			0.2490		0.88		
5		3.9125			0.2579		0.91		
Average				96.7		4.68	0.90	10	53
Average deviation				0.1		0.01	0.02	0.6	3
Average	0.0150							6	53
Average deviation								0.4	3
1	0.0200	4.3180	3.9810	92.2	1.2633	4.02			
2		4.3121	3.9493	91.6	1.2594	4.01			
3		4.3884	3.9511	90.0	1.2920	4.04			
4		3.8998			0.1306		0.46		
5		3.6869			0.1127		0.42		
Average				91.3		4.02	0.44	5	37
Average deviation				0.8		0.01	0.02	1.7	7
1	0.0300	4.3550	3.7385	86.8	1.1951	3.77			
2		4.4029	3.7380	84.8	1.2124	3.78			

Table XVII. Continued.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of Keratin	pounds per inch	percentage
3		4.3980	3.7296	84.8	1.1978	3.74			
4		3.8274			0.1140		0.41		
5		4.4169			0.1646		0.51		
Average				85.1		3.76	0.46	3	37
Average deviation				0.4		0.02	0.05	0.1	3
1	0.0400	4.4108	3.4670	78.6	1.0958	3.41			
2		4.4270	3.3749	76.2	1.0843	3.36			
3		4.3907	3.4178	77.8	1.0741	3.36			
4		3.8927			0.1123		0.40		
5		3.6992			0.1069		0.40		
Average				77.5		3.38	0.40	2	33
Average deviation				0.9		0.02	0.00	0.5	3
1	0.0500	4.4533	3.2822	73.7	1.0237	3.16			
2		4.5310	3.2761	72.3	1.0406	3.15			
3		4.3114	3.0364	71.6	0.9742	3.10			
4		4.4742	3.2311	72.2	1.0276	3.15			
5		4.1042			0.1172		0.38		
6		3.3437			0.0878		0.36		
Average				72.5		3.14	0.37	1	33
Average deviation				0.7		0.02	0.01	0.7	3

Table XVII. Continued.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	molality	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	0.0600	4.4776	2.8266	63.1	0.8974	2.75			
2		4.4739	2.8083	63.0	0.9198	2.82			
3		4.4629	2.8494	63.9	0.9184	2.81			
4		4.5157	2.8926	64.1	0.9147	2.78			
5		4.0051			0.1074		0.36		
6		4.2039			0.0863		0.29		
Average				63.5		2.79	0.33	< 1	--
Average deviation				0.5		0.03	0.04	--	--

Table XVIII

Effect of fifty volumes of acidic potassium permanganate in ten hours at 40° C. on the total nitrogen of wool keratin.

Determination	Potassium permanganate: molality	Keratin: gram	Hydrochloric acid: molality	Hydrochloric acid: cc.	Sodium hydroxide: molality	Sodium hydroxide: cc.	Nitrogen: percentage of keratin	Nitrogen: percentage of residue
1	0.0100	4.4806	0.3150	200.00	0.2370	53.00	15.77	
2		4.5138	0.3305	175.00	0.2386	30.10	15.72	
3		4.4292				33.30	15.78	
Average							15.76	16.30
Average deviation							0.02	
1	0.0200	3.9310	0.3305	150.00	0.2386	36.05	14.53	
2		3.9290				35.40	14.66	
3		3.9470				33.80	14.73	
Average							14.61	16.04
Average deviation							0.08	
1	0.0300	4.3482	0.3150	150.00	0.2370	16.80	13.94	
2		4.4753	0.3305		0.2387	21.40	13.92	
3		4.4742				22.00	13.88	
Average							13.91	16.35
Average deviation							0.02	
1	0.0400	4.3320	0.3305	150.00	0.2387	30.50	12.94	
2		4.3151				32.10	12.87	
3		4.3694				29.85	12.91	
Average							12.91	16.66
Average deviation							0.02	

Table XVIII. Continued.

Determination	Potassium permanganate molality	Keratin gram	Hydrochloric acid molality	Hydrochloric acid cc.	Sodium hydroxide molality	Sodium hydroxide cc.	Nitrogen percentage of keratin	Nitrogen percentage of residue
1	0.0600	4.6036	0.3305	150.00	0.2336	40.95	12.10	
2		4.3112				54.90	11.85	
3		4.4360		151.00		50.00	11.99	
4		4.2326		150.00		57.50	11.87	
Average							11.90	16.41
Average deviation							0.08	
1	0.0600	4.4785	0.3305	150.00	0.2336	58.60	11.13	
2		4.2360				71.90	10.72	
3		4.4404		153.00		67.10	10.90	
Average							10.92	17.20
Average deviation							0.14	

Table XIX

Effect of 0.02 N acidic potassium permanganate in ten hours at 40° C. on the weight, sulfur, wet warp breaking strength, and elongation at breaking load of wool keratin.

Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	cc. per gram keratin	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	62.50	5.7089	4.9681	87.0	1.5777	3.80			
2		4.3073	3.8063	88.4	1.2139	3.87			
3		4.4147	3.8662	87.5	1.2585	3.91			
4		3.8910			0.1485		0.52		
5		4.1200			0.1808		0.60		
Average				87.6		3.86	0.56	4	40
Average deviation				0.5		0.04	0.04	0.4	7
1	75.00	4.7238	3.8769	82.0	1.2215	3.55			
2		4.9217	4.1103	83.5	1.2973	3.62			
3		4.8590	4.0097	82.5	1.2602	3.56			
4		4.0324			0.1431		0.49		
5		4.2774			0.1355		0.44		
Average				82.7		3.58	0.47	3	47
Average deviation				0.6		0.03	0.03	0.9	4
1	87.50	3.9575	3.1510	79.6	1.0113	3.51			
2		4.0526	3.2251	79.6	1.0594	3.59			
3		3.7963	2.9821	78.6	0.2724	3.52			
4		3.9478			0.1431		0.50		
5		3.9177			0.1391		0.49		
Average				79.3		3.54	0.50	<1	--
Average deviation				0.4		0.04	0.01	--	--

Table XIX. Continued.

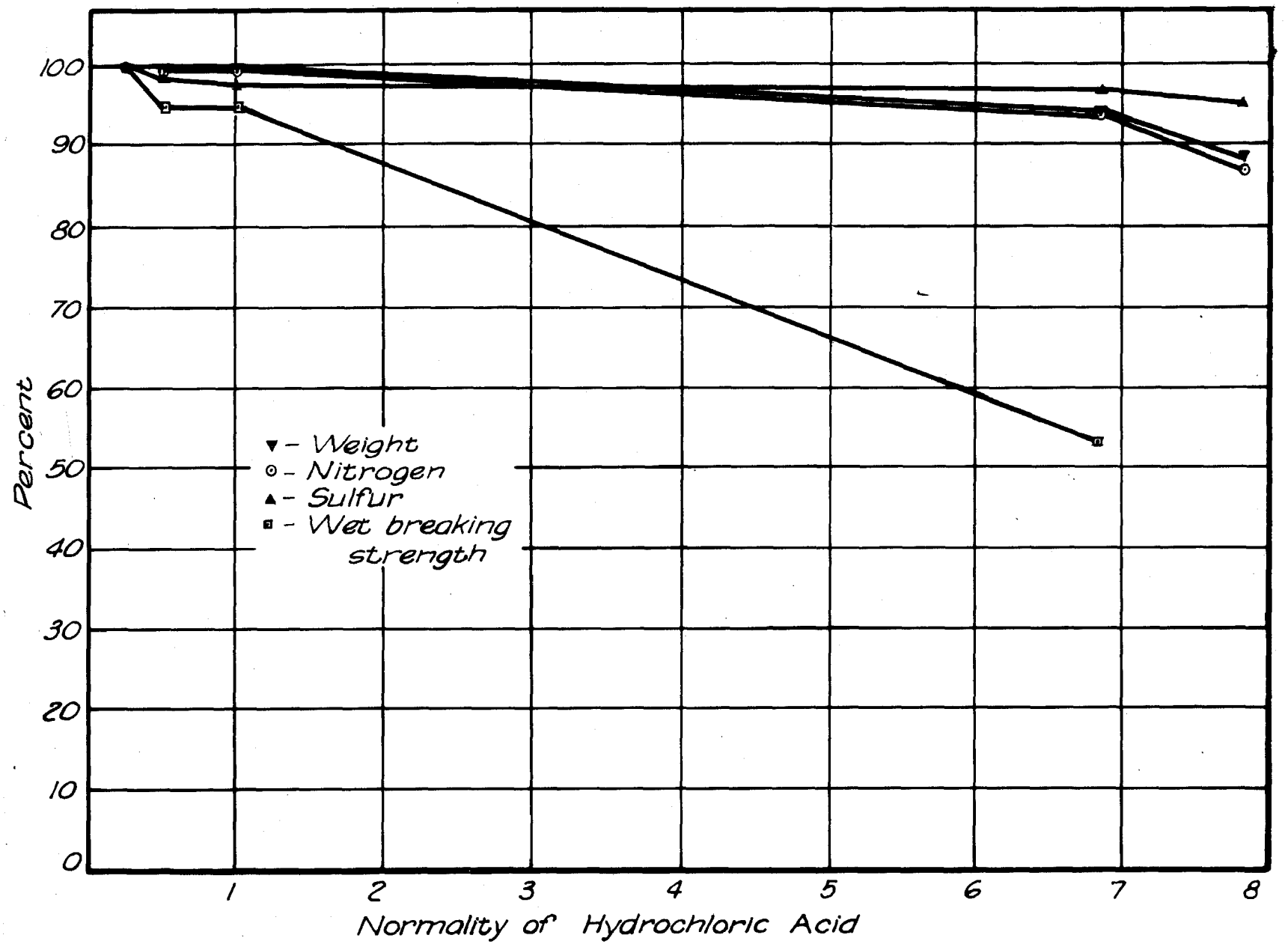
Determination	Potassium permanganate	Keratin	Residue		Barium sulfate	Total sulfur	Sulfate sulfur	Breaking strength of wet warp	Elongation at breaking load
	cc. per gram keratin	gram	gram	percentage of keratin	gram	percentage of keratin	percentage of keratin	pounds per inch	percentage
1	100.00	4.3825	3.3627	76.7	1.1052	3.46			
2		3.8797	3.0430	78.4	1.0033	3.57			
3		3.9067	3.0930	79.2	1.0049	3.53			
4		4.5658			0.1305		0.39		
5		4.5541			0.1389		0.42		
Average				78.1		3.52	0.42	<1	--
Average deviation				0.9		0.04	0.02	--	--

Table XX

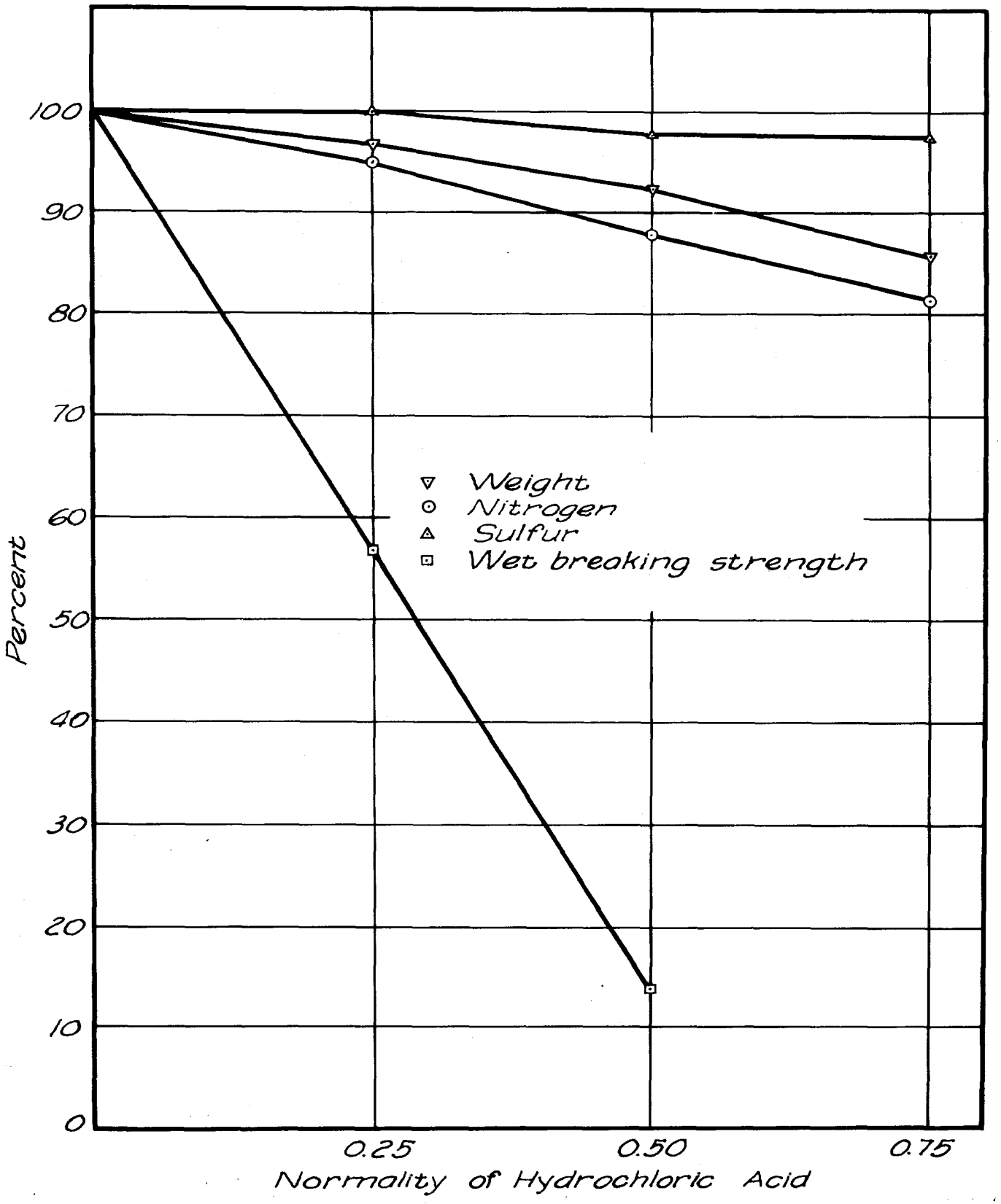
Effect of 0.02 N acidic potassium permanganate in ten hours at 40° C. on the total nitrogen of wool keratin.

Determination	Potassium permanganate: cc. per gram keratin	Keratin: gram	Sodium hydroxide*: cc. 0.2386 N	Nitrogen: percentage of keratin	Nitrogen: percentage of residue
1	62.50	4.3713	23.80	14.07	
2		4.4615	20.00	14.07	
3		4.2679	28.00	14.08	
Average				14.07	16.06
Average deviation				0.01	
1	75.00	3.7686	55.80	13.48	
2		4.0251	45.90	13.44	
3		4.3310	33.10	13.48	
4		4.5410	24.45	13.49	
Average				13.47	16.29
Average deviation				0.02	
1	87.50	4.6930	26.90	13.17	
2		4.4360	33.40	13.14	
3		3.9335	50.60	13.15	
Average				13.15	16.58
Average deviation				0.01	
1	100.00	3.8850	60.70	12.65	
2		4.4634	39.40	12.61	
3		4.4051	41.40	12.62	
4		4.4664	38.50	12.67	
Average				12.64	16.18
Average deviation				0.02	

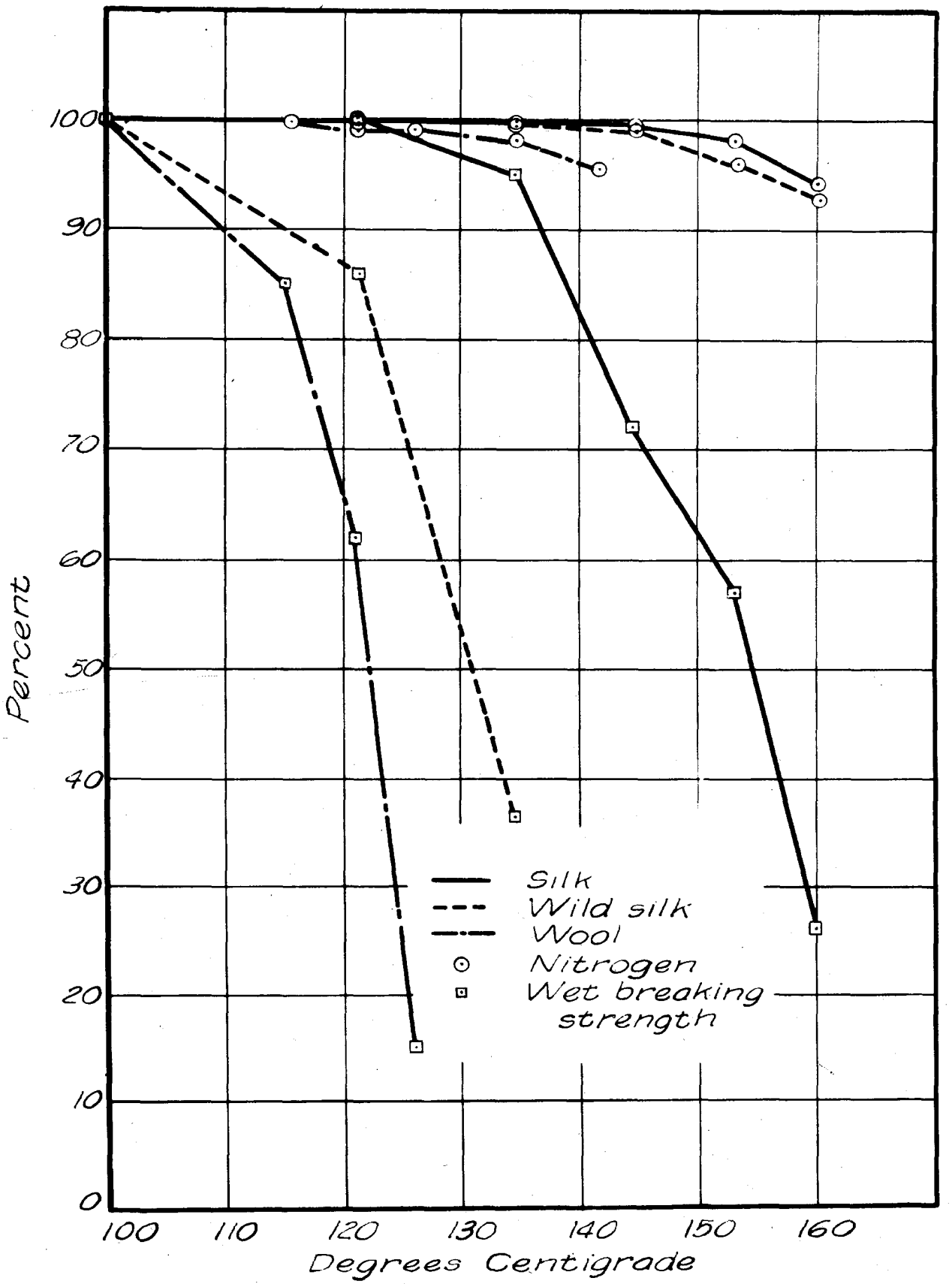
*The ammonia was distilled into 150.00 cc. 0.3306 N hydrochloric acid.



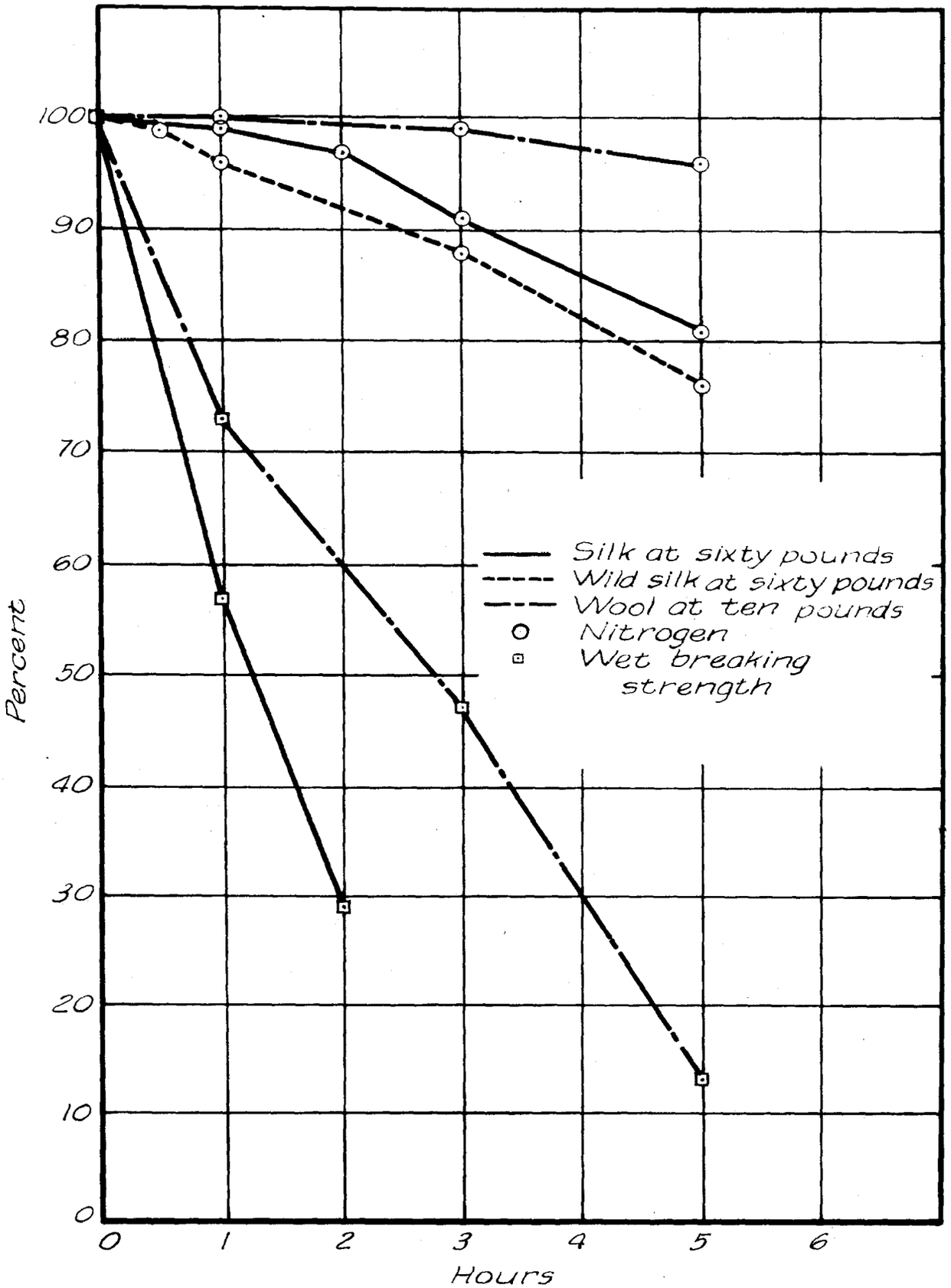
Graph I. Effect of acid in ten hours at 250 C. on the weight, nitrogen, total sulfur and wet breaking strength of wool.



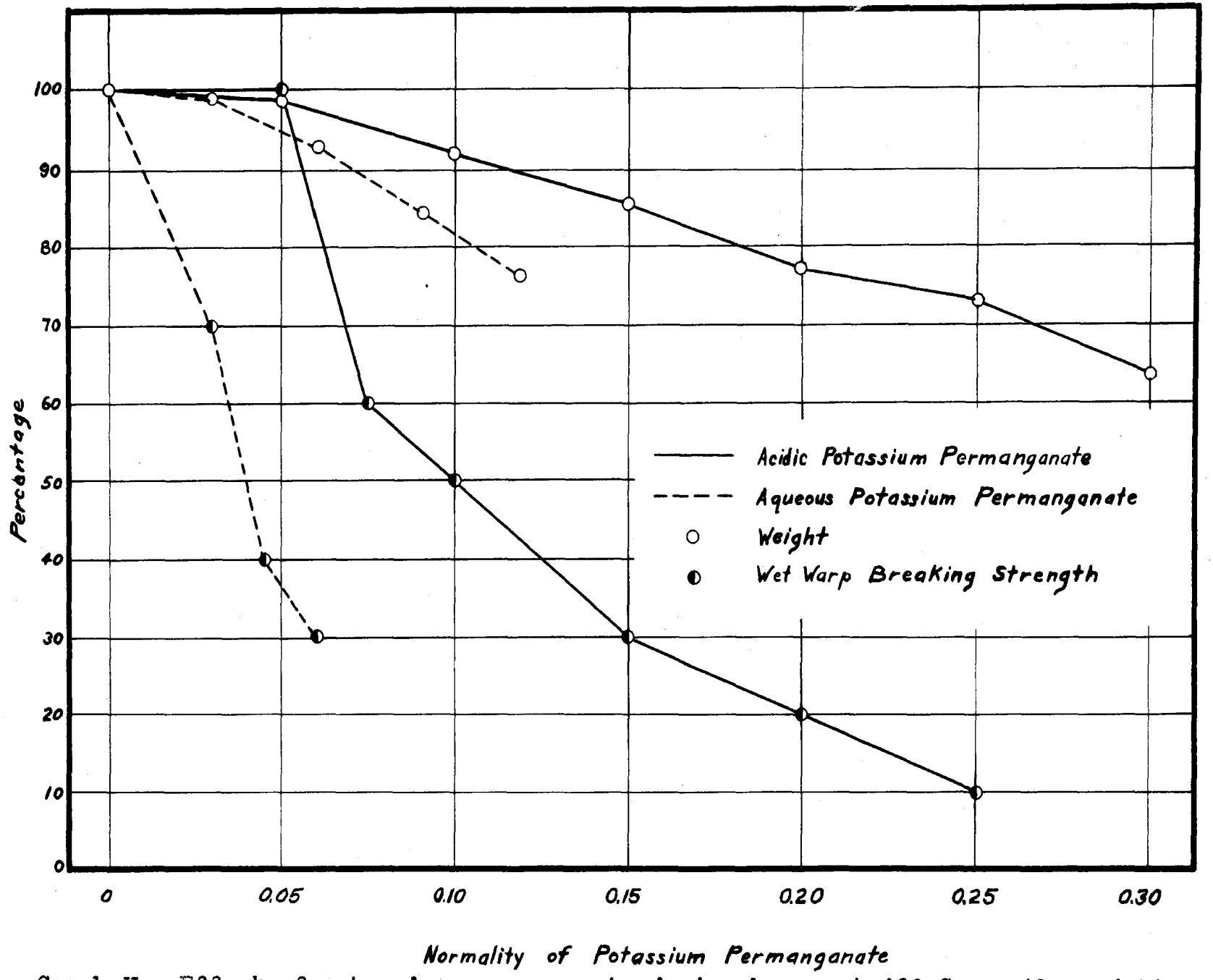
Graph II. Effect of acid in one hour at 100° C. on the weight, nitrogen, total sulfur and wet breaking strength of wool.



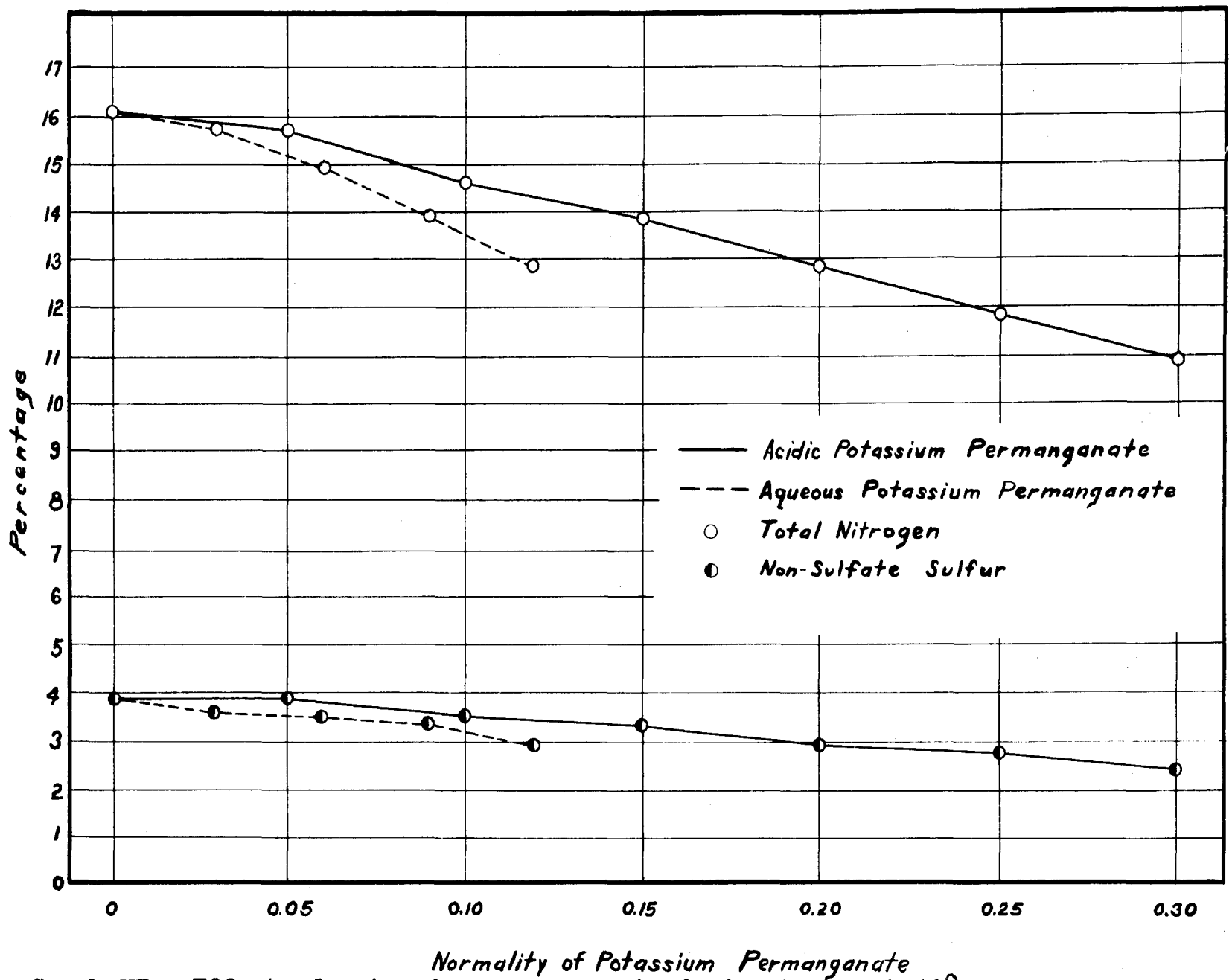
Graph III. Effect of steam in one hour on the nitrogen and wet breaking strength of silk, wild silk, and wool.



Graph IV. Effect of time of steaming on the nitrogen and wet breaking strength of silk and wild silk at 60 pounds and wool at 10 pounds per square inch.



Graph V. Effect of potassium permanganate in ten hours at 40° C. on the weight and wet breaking strength of wool.



Graph VI. Effect of potassium permanganate in ten hours at 40° C. on the total nitrogen and non-sulfate sulfur of wool.

DISCUSSION OF RESULTS

The effect of dilute hydrochloric acid at 25° C. for 10 hours and at 100° C. for one hour, of concentrated hydrochloric acid at 25° C. for 10 hours, of sodium chloride at 100° C. for one hour, of steam at 100° to 141.5° C. for one hour and at 115.2° C. for one to five hours, of sodium hydrogen sulfite at 40° C. for 10 hours and of aqueous and acidic potassium permanganate at 40° C. for 10 hours on the weight, nitrogen, total sulfur and sulfate sulfur of wool keratin is presented in tables and graphs. Since a 50 per cent loss in original strength of fabric is one criterion of its failure for use (56), tests of the wet mechanical performance of the residual fabric have been made.

Dilute hydrochloric acid at 25° C. for 10 hours is shown in graph 1 to have but slight effect on the weight, total sulfur, total nitrogen or wet strenth of wool (these results agree with those previously reported for the effect of acids on the strength of wool, 50, 68, 99, 122, 150). Concentrated hydrochloric acid at 25° C. for 10 hours is shown in graph 1 to bring about appreciable decrease in the weight and total nitrogen, approximately 50 per cent decrease in the strength and only a slight decrease in the total sulfur of wool.

Degradation of wool keratin by dilute hydrochloric acid at 100° C. for one hour is shown in graph 2 to increase with increasing concentration of acid, the wet strength to decrease more rapidly than either weight or nitrogen and the total sulfur to remain almost unchanged. The residual wool decreases slowly in nitrogen and increases slowly in sulfur.

It is shown that 0.06 M sodium chloride at 100° C. for one hour causes a slight loss of nitrogen by wool.

Steaming is shown in graphs 3 and 4 to have a very detrimental effect on wool, the wet strength decreasing very rapidly with increasing pressure or time. The first appreciable loss in both sulfur and nitrogen occurs at 134.5° C., a temperature at which the wool becomes very brown and friable. This temperature is lower than that of 140° C. reported for the first evolution of sulfur-containing gases from wool (115). The weight, total sulfur and nitrogen of the wool decreased more slowly than its wet strength which is only 16 per cent of the original after one hour at 126° C. Heating in an oven at 100° C. for 18 hours was found to cause no appreciable loss in wet strength and an increase of eight per cent in dry strength compared to the strength of wool conditioned six hours; 21 days in a desiccator also caused an eight per cent increase in the dry strength of the wool.

Sodium hydrogen sulfite, 0.9525 M, in 10 hours at 40° C. is shown to cause no loss in weight and a slight increase in

the nitrogen and sulfur of wool although it decreases the wet strength 50 per cent. This loss in strength confirms results obtained by Udalm and Rinoldi (112, 114). Goddard and Michaelis (53) formulated the reaction between sulfurous acid and cystine as, $R-S-S-R + H_2SO_3 = R-S-H + R-S-SO_3H$ A reaction of this nature which ruptures a disulfidic linkage may account for the loss in strength. The increase in total sulfur is doubtless explained by adsoprtion of sodium hydrogen sulfite; the analysis for sulfate sulfur yielded 0.86 per cent compared to 0.93 per cent in the case of the blank.

The effect on wool of 50 volumes of 0.01 to 0.04 N aqueous potassium permanganate and of 0.01 to 0.06 M acidic potassium permanganate in 10 hours at 40° C. is summarized in tables XXI and XXII. Percentage losses in weight, nitrogen and non-sulfate sulfur appear quite similar if magnification of the differences in conversion of percentages of keratin to percentages of weight, nitrogen and sulfur, respectively, of the blank be considered (multiples for nitrogen range from 6 to 9, for non-sulfate sulfur from 21 to 41, and for sulfate sulfur from 102 to 303). The strength of the wool is shown in graphs 5 and 6 to decrease much more rapidly in the aqueous than in the acidic solution and the weight, total nitrogen and non-sulfate sulfur are shown to decrease less rapidly than the strength and at nearly the same rate in acidic as in aqueous solution. The lower total sulfur of wool treated in acidic potassium permanganate is explained by removal of part of the sulfate sulfur;

percentages of sulfate sulfur yielded by the wool are:

A. Molality	0.00	0.01	0.02	0.03	0.04	0.05	0.06
Aqueous	0.93	0.92	0.82	0.90	0.90		
Acidic	0.93	0.90	0.44	0.46	0.40	0.37	0.33

B. Volume 0.02 M $KMnO_4$	50	62.5	75	87.5	100
Aqueous	0.82	0.90	0.87	0.98	0.94
Acidic	0.44	0.56	0.47	0.50	0.41

The effect of varying the volume of 0.02 N potassium permanganate in 10 hours at 40° C. is summarized in tables XXIII and XXIV. The weight, nitrogen, non-sulfate sulfur and wet strength are shown to decrease with increasing volume; the decrease in strength is again more rapid in the aqueous than in the acidic solution.

The same concentration of acid was used in all acidic solutions of potassium permanganate since the oxidation potential is a function of the hydrogen-ion concentration (31).

$$MnO_4^- + 8\ H^+ + 5\ e \longleftrightarrow Mn^{++} + 4\ H_2O$$

$$E_{MnO_4^-} = E_{o_{MnO_4^-}} + \frac{0.060}{5} \log \frac{[H^+]^8 [MnO_4^-]}{[Mn^{++}]} \quad \text{at } 30^\circ \text{ C.}$$

The concentration chosen, 0.18 N sulfuric acid, was that required for the highest concentration of potassium permanganate, 0.06 N, according to the equation,

$$2\ KMnO_4 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ [O]$$

This gives a range from 0.04 N alkali to 0.18 N acid for the solutions of potassium permanganate.

Although residual wool keratins from treatment with other oxidants have been reported to contain sulfate equivalent to part of their original sulfur (23, 123) in no case was the sulfate sulfur of wool increased by potassium permanganate in this study. The residual keratin from treatment with 50 volumes of 0.06 M acidic potassium permanganate for 10 hours at 40° C. yielded 0.48 per cent and the blank 0.01 per cent ash.

The similar losses of weight, nitrogen and non-sulfate sulfur seem to indicate that solution of the entire wool substance is taking place at the surface of the fiber rather than elimination of portions containing different ratios of sulfur to nitrogen. The greater rate of loss in strength by wool in the aqueous solution may be partly explained by the action of the alkali formed in the complete decomposition of the potassium permanganate,

$$2\ KMnO_4 + HOH = 2\ KOH + 2\ \underline{MnO_2} + 3\ [O]$$

for 0.01, 0.02, 0.03 and 0.04 M solutions of sodium hydroxide in 10 hours at 40° C. have been shown to bring about 10, 25, 40 and 50 per cent losses of strength in wool (15).

Although aqueous solutions of potassium permanganate are more commonly used in the processing of wool, acidic solutions are shown to be more desirable and a specification of volume as well as concentration of oxidant necessary.

Table XXI

Effect of fifty volumes of potassium permanganate in 10 hours at 40° C. on the weight, total nitrogen, non-sulfate sulfur, and wet warp breaking strenth of wool keratin.

Potassium permanganate molality	Weight		Nitrogen		Non-sulfate sulfur		Breaking strength of wet warp	
	aqueous	acidic	aqueous	acidic	aqueous	acidic	aqueous	acidic
	percentage of wool keratin						pounds per inch	
0	98.9	98.9	16.11	16.11	3.75	3.75	10	10
0.0100	96.7	96.7	15.70	15.76	3.62	3.78	7	10
0.0150							4	6
0.0200	92.3	91.3	14.94	14.64	3.55	3.58	3	5
0.0300	83.9	85.1	13.96	13.91	3.36	3.30	<1	3
0.0400	76.3	77.5	12.27	12.91	2.94	2.98		2
0.0500		72.5		11.90		2.77		1
0.0600		63.5		10.92		2.46		<1

Table XXII

Percentage loss of weight, total nitrogen, non-sulfate sulfur, sulfate sulfur, and wet warp breaking strength of wool keratin after ten hours in fifty volumes of potassium permanganate.

Potassium permanganate molality	Weight		Total nitrogen		Non-sulfate sulfur		Sulfate sulfur		Breaking strength of wet warp	
	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic
0.0100	2	2	3	2	4	+1	1	3	30	0
0.0150									60	40
0.0200	7	8	7	9	5	5	12	53	70	50
0.0300	15	14	15	14	10	12	3	51	100	70
0.0400	23	22	20	20	22	21	3	57		80
0.0500		27		26		26		62		90
0.0600		36		32		34		65		100

Table XXIII

Effect of 0.02 M potassium permanganate in ten hours at 40° C. on the weight, total nitrogen, non-sulfate sulfur, and wet warp breaking strength of wool keratin.

Potassium permanganate cc. per gram keratin	Weight		Nitrogen		Non-sulfate sulfur		Breaking strength of wet warp	
	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic
	percentage of original fabric						pounds per inch	
50.00	92.3	91.3	14.04	14.64	3.55	3.58	3	5
62.50	89.6	87.6	14.43	14.07	3.40	3.30	<1	4
75.00	85.9	82.7	13.09	13.47	3.13	3.11	--	3
87.50	80.6	79.3	13.44	13.15	2.92	3.04	--	<1
100.00	76.3	76.1	12.89	12.64	2.83	3.10	--	--

Table XXIV

Percentage loss of weight, total nitrogen, non-sulfate sulfur, sulfate sulfur, and wet warp breaking strength of wool keratin after ten hours in 0.02 N potassium permanganate at 40° C.

Potassium permanganate cc. 0.02 N $KMnO_4$ per gram keratin	Weight		Nitrogen		Non-sulfate sulfur		Sulfate sulfur		Breaking strength of wet warp	
	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic	Aqueous	Acidic
50.0	7	8	7	9	5	8	12	58	70	50
62.5	11	11	10	13	9	12	5	40	100	60
75.0	15	16	13	16	17	17	7	50		70
87.5	19	20	17	18	22	19	+5	46		100
100.0	24	21	20	22	23	17	+1	56		

SUMMARY

1. The degradation of wool keratin by 0.25 to 7.87 N hydrochloric acid in 10 hours at 25 ° C. and by 0.25 to 0.75 N hydrochloric acid in one hour at 100° C. has been followed by weight, nitrogen, sulfur, and wet warp breaking strength of the residual keratin. Acid degradation has been shown to be much greater at 100° C. than at 25° C., to remove little of the sulfur, and to decrease the wet strength more rapidly than the weight or nitrogen. The residual wool has been shown to decrease in nitrogen and increase slowly in sulfur with increasing concentration of acid.

2. The degradation of wool keratin by 0.06 or 0.70 N sodium chloride in one hour at 100° C. has been shown in the same manner to be very slight.

3. The degradation of wool keratin by steam at 100° to 141.6° C. in one hour and by steam at 115.2° C. in one to five hours has also been followed by analysis of the residual keratin for weight, nitrogen, sulfur, and wet strength. Degradation by steam has been shown to increase with increasing pressure or time; wet strength, which disappears in one hour at 134.6° C., has been shown to decrease more rapidly than weight, nitrogen or sulfur.

4. The degradation of wool keratin by 0.9825 M sodium hydrogen sulfite in 10 hours at 40° C. has been followed by weight, nitrogen, total sulfur, sulfate sulfur and wet strength. The residual wool from this treatment analyzed only slightly higher in nitrogen and total sulfur and slightly less in sulfate sulfur but retained only 50 per cent of its original wet strength.

5. The degradation of wool keratin by 50 volumes of 0.01 to 0.04 M aqueous potassium permanganate, by 50 volumes of 0.01 to 0.06 M acidic potassium permanganate, by 50 to 100 volumes of 0.02 M aqueous potassium permanganate, and by 50 to 100 volumes of 0.02 M acidic potassium permanganate in 10 hours at 40° C. has been followed by weight, nitrogen, total sulfur, sulfate sulfur and wet strength of the residual keratin. Percentage decreases in weight, total nitrogen, and non-sulfate sulfur have been shown approximately the same in aqueous and acidic solutions. Solution of part of the sulfate sulfur has been shown to occur in acidic potassium permanganate. Wet strength has been shown to decrease more rapidly than weight, nitrogen, or sulfur and more rapidly in aqueous than in acidic potassium permanganate.

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