

Review of Analytical Work Applicable to Leather and Tanning, 1920-1921¹

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PROBABLY few, if any, of our important industries offer to chemists as fertile a field for research and scientific work as does that of tanning. Certainly in no other industry is so little known of the composition of the principal raw materials and of the mechanism and control of the fundamental processes. In the past few years, however, there has been an increasing interest and activity in leather and tanning chemistry which is indeed gratifying, and it is hoped this will continue until the art of tanning has been put on a sound scientific basis.

Many problems of analytical nature are still unsolved and probably will remain so until there is a better knowledge of the fundamentals involved. Progress in this branch, however, can certainly be claimed, as will be readily realized from the following review of work done in the short space of two years.

TANNIN ANALYSIS

In this country the work of Wilson and Kern on the hide powder method of tannin analysis has redirected attention to fully recognized sources of error in this method and has also revived considerable interest in the subject by the rather startling results obtained. In their first paper²,* they describe a method which consists essentially of shaking the tannin solution with purified hide powder until all tannin, as determined by the gelatin-salt test, has been removed from solution. The tanned hide powder is then washed free from soluble matter, dried, and analyzed for tannin as in the regular procedure for vegetable tanned leathers, and from this figure the percentage of tannin in the original material is calculated. Figures from comparative analyses of 8 common tanning materials by this new method and by the official hide powder method of the American Leather Chemists Association are from 43 per cent to 220 per cent higher for tannin by the latter method, due chiefly to the removal by this method of nontannins, such as gallic acid, pyrocatechol, and so on, which do not make leather and are readily washed out. The presentation of Wilson and Kern's paper brought forth considerable discussion² in opposition to it and also quite a controversy between the authors and Schultz and Blackadder.

The two last-named authors³ in a detailed study of the new method take exception to several assumptions involved in it and give data to indicate that two are in error: namely, "that there is a definite chemical compound formed between the tannin in the tannin solution and the collagen in the hide powder during a 6-hr. shaking, which chemical compound is stable with regard to water and also insoluble in water;" and "that one definite chemical compound is formed throughout the whole of the hide powder used in the analysis." They show particularly that from the washings of the tanned hide

powder a certain amount of tannin can be recovered as determined by the new method and that the tanned hide powder is very heterogeneous physically, being made up roughly of a distinctly fibrous portion and a relatively fine powdery portion. The last is more heavily tanned than are the coarser particles and being so very fine is apt to be lost during washing. The loss of this relatively tannin-rich powder leaves the residue proportionally poorer in tannin and causes a loss of tannin as determined by the new method.

In further defense of their new method Wilson and Kern⁴ give data to show that tannin once combined with hide cannot be washed out by any amount of washing that would be practical, and that concentration of the nontannins and washings from the tanned hide powder converted certain nontannins into substances capable of tanning.

In continuation of the controversy Schultz⁵ presented a very elaborate study showing that the detannized solution and washings according to Wilson and Kern's method contain materials which, without concentration, will combine with hide powder and be resistant to washing. An experiment is also described which indi-

cates that concentration does not bring about a chemical change with conversion of nontannins into tanning materials, and according to Schultz such phenomena are probably explained by the dispersed state of the tannin under various conditions. Results from a rather extensive series of experiments, involving a strict comparison of the basic principles of the official hide-powder method and of the new one, show that the effects of the three factors influencing the absorption of tannin by hide powder, namely, the amount of hide powder, concentration of tannin, and volume of solution, are as pronounced after washing the tanned hide powder as they are without washing. Schultz concludes that the Wilson and Kern method of tannin analysis is based on a series of false assumptions and gives neither the true value of tanning materials nor the true tannin content.

Since considerable objection was raised to the Wilson and Kern method on the ground that it was too cumbersome and time-consuming, these two authors presented a modification⁶ which greatly simplified their procedure and also removed several possible sources of manipulative errors which previously had been pointed out. Comparative analysis, by the original and revised procedures, however, of 6 typical extracts gives practically identical results. Replying to the work of Schultz, Wilson and Kern⁷ refute many of his objections and particularly show that the new method will give the same tannin figure for varying quantities of hide powder. Answering this paper Schultz⁸ gives further argument against the work of Wilson and Kern and in support of his findings.

Baldracco and Camilla⁹ have proposed a modification of the official method of tannin analysis of the Society of Leather



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* Numbers in the text refer to Bibliography at end of paper.

Trades' Chemists using a prepared, lightly chromed hide powder. It is contended that the usual washing of hide powder removes acid which is necessary for complete combination of the tannin and hide powder, and that ready chromed hide powder as prepared by them¹⁰ always contains sufficient acid for complete detanning and is much more convenient to use. Schell¹¹ in criticism of the work of Baldracco and Camilla states that their tannin figure includes more nontannin than in the case of the official method and that their method is not as exact nor is the hide powder they propose as well defined as the official one. Lauffmann¹² claims that the reagents used by Baldracco and Camilla are not suitable as they give similar reactions for tannins, and also that proof has still to be produced that hide powder with the filter method absorbs materials which should really be estimated as nontannins. In reply Baldracco and Camilla¹³ point to their previous work showing that tanning by the filter method is too high as some nontannins are absorbed, while by the official shake method of the International Association of Leather Trades' Chemists the tannic acid is not all removed from certain extracts.

Moeller^{14,15} has done considerable work on the error in nontannin determinations due to the presence of hydrolyzed hide substance. Determination of the dissolved hide substance in the nontannin residues from about 50 tanning materials showed that it usually amounted to several per cent of the nontannin residue. Parker and Terrell¹⁶ in some notes on the filtration of tanning solutions show the superiority of the filter candle to filter paper, as the latter continues to absorb soluble matter even after considerable quantity of solution has passed through. Thompson, Seshachalam, and Hassan¹⁷ have shown that in tannin analysis the time of filtration, color, tannin content, insolubles and so on are all liable to considerable variation with different degrees of acidity. Sollmann¹⁸ in studies on the precipitation of proteins by tannin has determined that in concentration (0.1 to 0.5 per cent) necessary to produce astringent action, precipitation is greatest at a pH of 2 to 5. There is no precipitation when the alkalinity is pH 8 to 8.3.

Frey and Clarke¹⁹ have proposed a practical simplification and shortening of the washing of chromed hide powder for tannin analysis and give data to show that results are in agreement with those from official practice. The report of the British tannin analysis committee²⁰ shows that in washing the chromed hide powder only distilled water should be used. Baldracco and Camilla¹⁰ have described the preparation of a ready chromed hide powder.

LEATHER ANALYSIS

VEGETABLE TANNED LEATHERS—A committee of the American Leather Chemists' Association under the chairmanship of Small²¹ has gone very thoroughly into the subject of the sampling of leather and its preparation for analysis. This excellent report gives complete analysis of the leather from all parts of hides and sides of various tannages, thus emphasizing the variations in composition and showing what sections to combine for the most representative sample. From these data a chart has been prepared showing the locations for sampling of all commercial trims. A French committee on leather analysis, with Chambard²² as chairman, has also done some work which shows a large zone between the shoulder and butt of nearly constant composition and recommends sampling in this section.

Veitch and Jarrell²³ in a detailed study of the determination of moisture in leather show particularly the influence of atmospheric humidity. With ungreased leathers a difference of 35 per cent relative humidity gives on the average a difference of 0.5 per cent in drying losses. It is also shown that repeated drying of leather at constant humidity gives a

progressive loss in weight; that the electric oven at 100° C. gives results slightly higher than the combined evaporator and drier; and that the vacuum oven at 70° C. gives results lower than the drier or electric oven at 100° C., but at 97° to 98° C. gives higher results.

The determination of hide substance in leather has been studied by several workers. Chambard²⁴ considers incomplete oxidation and too small a charge of leather as the most likely sources of error. He obtains good results with a modification of the Kjeldahl method as for silk analysis using a relatively large sample (2.8 g.) of leather and digesting with sulfuric acid, potassium bisulfite, and anhydrous copper sulfate. F. G. A. Enna²⁵ proposes a rapid method using a drop of mercury which is afterwards precipitated out. Cochran²⁶ from work on feeds and feces, shows that the addition of permanganate does not cause a loss of nitrogen and that using the same method without the addition of permanganate results are less concordant and uniformly lower. Kahn²⁷ considers as important sources of error in the Kjeldahl method the following: lack of uniformity of the powdered leather; insufficient decomposition; the possibility of alkali, acid or particles of zinc being carried over in the distillation; and of some ammonia escaping with the air bubbles. Parker and Terrell²⁸ have investigated the use of perchloric acid in Kjeldahl digestions of leather and have found that it gives satisfactory results and considerably shortens the time of digestion.

Active work both here and abroad has been continued on the much-mooted question of a suitable solvent for the extraction of oils and greases from leather. Two English committees²⁹ have compared numerous solvents from which they conclude that either chloroform or benzene should be officially adopted with preference for the latter if the color of the extract is of importance. Veitch and Clarke³⁰ have summarized previous work on the subject and give data on the extraction, particularly of soaps, in leather. It is shown that the presence of moisture increases the quantity of soap fats extracted by chloroform and petroleum ether; that the presence of tannic acid increases the solubility of soap fats very greatly, especially in chloroform; that magnesium salts added to leather will lead to the extraction of the soap as a whole if opportunity is given for the formation of magnesium soaps, since these are very soluble in both chloroform and petroleum ether; and that calcium soaps are extracted by chloroform in a colloidal state but are practically insoluble in petroleum ether.

A committee report of the American Leather Chemists' Association by Terrassee and Anthes³¹ on water-solubles in leather gives the results of a study of the official method from which it is concluded that the sample should be finely ground and freed from grease and that the extraction should be carried out in a specified apparatus on 30 g. of leather at 50° C. Two liters of extract should be collected in three hrs. without any previous period of soaking. A later committee under the chairmanship of Wilson³² undertook to study primarily the influence of temperature and whether or not a definite endpoint could be reached in the water extraction of leather. The committee results showed very little agreement on these two points. Apropos of the subject, Veitch and Frey³³ have published some notes showing that there is no absolute endpoint even for a 148-hr. extraction but that the extraction appears to settle down to a practically constant value.

A subject for considerable work has been the determination of glucose in leather. Rogers³⁴ as chairman of an American Leather Chemists' Association committee made quite an elaborate report showing that five drops of toluene per liter will preserve leather extracts for at least three days without loss of sugar; that when sodium carbonate is used for neutralization

after hydrolysis in the presence of Epsom salts high results are obtained because of the precipitation of magnesium; that caustic soda if used in excess will precipitate the magnesium; that there does not appear to be any advantage in using stronger solutions for analysis; and finally, a point of considerable importance, that low results when using sodium hydroxide for neutralization are possibly not due to any action of the sodium hydroxide on the dextrose but to sodium plumbite which has a reducing action on the sugar. Continuing his committee work, Rogers³⁵ sought the best reagent for complete removal of lead and as a result recommended that a strong solution of disodium acid phosphate be made the object of further study. To shorten the time for sugar determination van der Hoeven³⁶ has proposed a volumetric procedure which is a modification of Schoorl's method. Quisumbing and Thomas³⁷ have made a very thorough, careful study of conditions affecting the determination of reducing sugars and have proposed a procedure which eliminates most sources of error.

In the determination of magnesium in leather Frey³⁸ has shown that Epsom salts determined from the ash of the leather ranges from 0.05 per cent to 0.25 per cent higher than when determined from the water extract and also that Epsom salts either alone or in solution in the water extract loses practically 40 per cent of its weight upon 16 hrs.' drying in the evaporator and dryer. The work of an American Leather Chemists Association committee with Frey³⁹ as chairman has shown that the volumetric procedure for magnesium as outlined by Handy gives results in agreement with those by the gravimetric method.

For the determination of sulfuric acid in leather Thomas⁴⁰ has proposed quite a departure from the usual suggestions. The principle of his method is based on the displacement of the sulfuric acid by ions of a higher valence and is effected by digestion of the leather with potassium dihydrogen phosphate solution. A modification of this same method is also given by Thomas and Frieden⁴¹ for the determination of hydrochloric acid and neutral chlorides in leather.

MINERAL TANNED LEATHERS—Hou⁴² in some experiments on the volumetric determination of chromium in leather by the sodium peroxide fusion method has emphasized the need of taking the fusion solution down to a small volume to insure decomposition of all peroxide and also of controlling the acidity of the solution for titration. An English committee, of which Innes⁴³ was chairman, has reported on methods which they have so far found best for the analysis of chrome leather. Brgeniner⁴⁴ has made a detailed study of the methods and factors influencing the determination of chromium.

Grasser,⁴⁵ one of the pioneer workers in iron tanning, has published a quite complete article on the subject and given methods for control analysis.

VEGETABLE TAN LIQUORS—Claffin⁴⁶ has proposed a very practical method for determining the plumping power of tanning solutions, which consists essentially of measuring the volume of solution absorbed by hide powder under properly controlled conditions. The simplicity of his method, together with the practical value of results by it, has proved very attractive. Working along the same line McLaughlin and Porter,⁴⁷ using pieces of limed and hydrated steer hide instead of hide powder, have made a study of the swelling of white hide in tan liquors, dealing particularly with the usual organic acids and calcium acetate and lactate. Their results emphasize the significance of direct results obtained in this manner. Atkin and Thompson⁴⁸ have published a very informing paper on the determination and control of the acidity of tan liquors by a colorimetric method using indicators.

Blackadder,⁴⁹ in a report on the color measurement in tanning solutions, describes some experiments with a tint photometer, from which he is inclined to conclude that any use of blue in a combination of color to match a tanning solution is unnecessary and may lead to error; and that while an apparatus based on matching a built-up color standard against an unknown color will not prove satisfactory, a machine based on spectrum analysis ought to be capable of adaptation. Wilson and Kern⁵⁰ have shown an interesting relation between the hydrogen-ion concentration of a tan liquor and its color value. Tan liquors change in color with change in pH value over a range from 3 to 12 and this change in color is completely reversible if the liquors are not long exposed to air. Liquors exposed to air continue to darken, with accompanying rise in the pH value, but this change is not reversed by lowering the pH value. Exposed to air at pH values of about 9, liquors give bulky precipitates when their pH values are brought to 3.

CHROME LIQUORS

The analysis of chrome liquors has apparently been a subject of considerable interest. Thomas and Foster⁵¹ have described a conductance-barium hydroxide titration method for chrome liquors which "is to be preferred to the American Leather Chemists Association titration method not only on account of theoretically truer results but also convenience." Adsorbed chromic sulfate in the precipitated hydrous chromic oxide is the chief cause of low results by the American Leather Chemists Association titration method. Dhavale and Das,⁵² from detailed experiments incidental to an investigation of the effect of neutral salts on the basicity of chrome liquors, have shown that the addition of sodium chloride causes a marked increase in the acidity of chrome liquors as found by the Procter and McCandlish method and also that the values obtained by this method are influenced by the temperature of titration and speed of adding the alkali but not by the dilution of the liquor under titration. Thomas and Foster⁵³ also deal with the effect of salt on the titration of chrome liquors and give some data which indicate that the alkalimetric titration method for acidity of chrome liquors could be made to yield more correct results by the addition of about 50 g. of sodium chloride before titrating. Burton and Hey,⁵⁴ in the course of investigations on chrome tanning, have pointed out the influence of carbon dioxide, sulfur dioxide, and volatile acids on the American Leather Chemists Association method of titrating acidity of chrome liquors, showing that it is inadequate since it fails to take these into account, and they have recommended that the titration be made by adding the caustic soda to the diluted liquor in the cold and by continuing the addition of alkali during the period of heating up to the boiling point. Pickering⁵⁵ has pointed out several precautions to be taken in determining basicity figures for chrome liquors, describing also a means of illumination for a clear end-point in titrating. Schorlemmer⁵⁶ and Grasser⁵⁷ have both discussed and suggested systems for expressing the basicity of chrome liquors. Thomas and Kelly⁵⁸ have proposed a rapid estimation of chromium in chrome liquors by means of the immersion refractometer.

LIME AND LIME LIQUORS—English committees on lime-ward control under Burton,⁵⁹ Atkin and Palmer,⁶⁰ Pickles,⁶¹ and Atkin and Atkin⁶² have been very active in reviewing, criticizing, and proposing methods best suited for lime liquor analysis. F. G. A. Enna⁶³ has described a method for determining the available sulfide in a lime liquor based on the fact that a quantitative separation of hydrogen sulfide from its alkaline salts is effected by carbonic acid, while thiosulfates and amino acids are unaffected. Singer⁶⁴ has made a comparative study of various methods for analysis of lime liquors.

Grasser⁶⁵ has pointed out the advantages of determining lime in un-haired skins from solution by wet oxidation rather than from solution of the ash. Veitch and Jarrell⁶⁶ have reviewed the various methods for determining available calcium oxide in lime and after considerable study have proposed and outlined in detail modifications of the tannery method and Scaife method so as to insure accurate and concordant results.

IDENTIFICATION OF TANNING MATERIALS

Grasser⁶⁷ has published some very interesting observations on the behavior of various tanning materials during electro-dialysis which may be developed for the identification of tannins. Lauffmann⁶⁸ has discussed in detail the tests for the identification and examination of tanning materials and extracts. Lauffmann⁶⁹ has also described a modification of the indophenol reaction so that it can be used for identification of that class of synthetic tannins formed by the condensation of formaldehyde with the sulfonic acids of phenol, cresol, naphthalene or anthracene.

De Hessel⁷⁰ has published a modification of Appelius and Schmidt's cinchonine test for sulfite-cellulose. With this test certain synthetic tannins react partially like vegetable tannins; others like sulfite-cellulose; and some do not give the reaction at all. Hough⁷¹ has described a method for determining bisulfites in extracts.

For differentiation between old fustic and quercitron extracts Justin-Mueller⁷² has found that the ether extracts upon solution in sulfuric acid and dilution with water remain bright orange-yellow for old fustic but are decolorized for quercitron. Atkin and Marriott⁷³ have shown that the application of polarized light in the microscopical analysis of sumac gives more definite and quicker results than does the ordinary microscopical procedure. Groll⁷⁴ has published considerable data on gambier and its adulteration, and Jablonski and Einbeck⁷⁵ have done likewise for quebracho, emphasizing particularly the value of a fluorescein reaction for its detection. Mimosa extract, however, gives a similar reaction.

SULFONATED OILS

A committee of the American Leather Chemists Association, with Schultz⁷⁶ as chairman, has made quite a study of the determination of combined SO₃, total fatty matter and neutral fat in sulfonated oils. Hart⁷⁷ has published a method and formula for the determination of inorganic impurities in sulfated oils, which formula he improved in a later paper.⁷⁸ Bunicke⁷⁹ has also offered an improvement of the Hart method. Pickering⁸⁰ has done considerable work on methods for the commercial examination of sulfonated oils. Kern⁸¹ has proposed the determination of sulfate in sulfonated oils by means of a solution of monosodium phosphate which will give a practically complete separation of oil from solution with sulfonated oil without the addition of a solvent and will extract all of the free and none of the combined sulfate.

MISCELLANEOUS

Thomas⁸² has described some experiments on estimating the tryptic activity of bating materials, using two methods developed from the work of Sherman and Neun. Matos⁸³ has discussed the testing of dyes in the leather industry. Weltwart⁸⁴ has given a method for determining ammonia in oil and fat preparations. Hoffman⁸⁵ has proposed a means of detecting and separating lactic acid as a complex sodium ferric lactate. Froboese⁸⁶ has dealt in considerable detail with the examination of leather substitutes. Bogue⁸⁷ has published a very comprehensive article on glues and gelatins, giving a most complete and excellent bibliography on the subject.

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