Evaluation of Modifications to the ALCA Standard Method for Tannin Analysis in Tannery Liquors*

by

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Abstract

The American Leather Chemists Association (ALCA) Standard Method for tannin analysis was developed to provide tanners with a way to monitor the relative strength of tan liquors in their process. Although it took full advantage of existing technology in the early 1900's, that method is very restrictive, laborious and time consuming. Advances in filtering technology allow modern researchers to process materials much more efficiently than in the past. Several filtration methodologies were incorporated into existing ALCA methods, and modifications were evaluated for time efficiency, effectiveness, and comparability to the Standard Methods. Direct determination of solids on undiluted tan liquor was evaluated against the Standard Method procedures.

Introduction

With the advent of chrome tanning in the early 20th century, the focus of ongoing research in the tanning industry came to decline concerning the use of vegetable tanning extract. However, vegetable tanned leather has maintained an important role in industry and society. The modern vegetable tanner faces many new challenges.[1,2] These challenges include the evaluation of recently developed materials and determination of a meaningful color rating for vegetable extract at a reasonable cost.

Operation of a vegetable tanning yard requires precise control of tannin concentration. Determination of tannin strength in the tanning vats is a difficult proposition. Daily measuring of tan liquor strength in the tannery is done using Barkometer. Barkometer, however, is purely a measure of density, or solids content (e.g. 100 Bk liquor = 1.100 specific gravity). While this process gives a relative strength of the tan liquor, it does not directly relate to tannin content. Older more depleted liquor has a lower tannin content than fresh liquor of the same Barkometer. The ALCA standard test method (Standard Method) for vegetable tannin analysis was developed to allow tanners to monitor very tightly the tannin concentration in their tanning vats. As the tanning process took several months to complete, the small daily shifts in tanning bath strength were critical to quality leather production. The Standard Method took advantage of technology available in the early 20th century to afford tanners a guide for running their tanyards in a controllable and efficient manner.[3]

The shorter tanning times in a modern vegetable tannery necessitate more rapid increases in tannin content through the tanyards. The higher gradient somewhat relaxes the need for two decimal point accuracy in the test procedures. The procedure for testing of the tan liquor strength, however, has remained virtually unchanged from that of the early 1900's. Review of the Standard Method reveals tight restrictions placed on nearly every facet of the testing procedures.

The ALCA method for tannery liquor analysis (A 25)[4] requires that the tannin solution be diluted to a prescribed concentration of 7 grams per liter of solids or maximum tannin concentration of 3.5 grams per liter. Obviously this data is not available until the analysis is complete, so there is a dilemma of how to prepare the solution in the proper concentration. If one has the history of the previous analytical data for a given vat or liquor, then an estimate is relatively easy to calculate for any given sample. However, lacking knowledge of previous analyses or current activity

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in the liquor, one must ascertain the solids prior to actual preparation of analytical solutions.

Different methods for solids determination were evaluated.

Filtration of tanning liquors for soluble solids and non-tan determination, by the Standard Method, requires the use of a specific filter paper (Schleicher & Schuell No. 610) and Kaolin, in a process lasting two or more hours per sample. Procurement of this particular filter paper in 2000-2001 proved to be easier said than done. After numerous telephone calls and follow-ups with the sole supplier, the material was finally special-ordered from Germany, at a cost several times higher than initially quoted. Elapsed time between ordering and receipt of the specified paper was three to four months. Obviously, a minor miscalculation of inventory or delivery time could leave a laboratory incapable to perform the required tests.

Non-tan determination by the Standard Method requires use of ALCA approved hide powder. Likewise, this material has a single supplier, as well. Because of delays in production during 2000-2001, receipt of required material was delayed by four to six months. Highly processed British hide powder was offered to another lab at a rate nearly 10 times the cost for standard material.

Contacting suppliers of the required cloth used for wringing out the hide powder proved impossible. Every listed supplier for the cloth is defunct. When potential vendors were queried about supplying cloth with the required thread count, company representatives did not have that information available. Short of obtaining multiple samples and personally doing a manual thread count, satisfying this requirement is nearly improbable.

By far the most time consuming part of the Standard Method is the filtration process. Processing times of two or three hours per set of samples are common. In an effort to make the process more time efficient, up-to-date filtering technology was evaluated for a viable alternative to the Standard Method. Different materials and methodologies were explored for repeatability and agreement with the Standard Method.

Literature Review

A review of existing literature was conducted to determine any pre-existing alternative methods for tannin analysis procedures. An alternative method of washing hide powder was studied[5] in 1920. Although the recommendation of the committee, including F. F. Marshall and W. K. Alsop, was to amend the Standard Method,[6] no change was ever made. An alternative JSLTC filtration method was developed in 1977 in response to the JSLTC method filter candles becoming unavailable.[7] Glass fiber filtration technology was successfully employed at that time.

As early as 1907 Reed[8] suggested to the ALCA committee on methods that a vacuum filtration would improve the tannin analysis method. By 1911 Oberfell[9] had indicated that a filter medium and apparatus had been developed that was adequate for vacuum filtration of tannin solutions as required by the ALCA methods. Unfortunately a quick glance at a picture of that apparatus suggests that the large, awkward glassware device might have been difficult to manage and clean. But now we can step forward almost 100 years into a time when plastics, inexpensive vacuum sources and widely diverse commercially available filtering media are readily and inexpensively available. The cumbersome, even dangerous, device used by Oberfell can be replaced by a small, durable and safe unit with greater practical utility. In fact a dozen collection stations with enclosed sample vials (to prevent evaporation) can easily fit into the same space taken by the original single filter device.

Experimental

Total solids determination

The easiest way to find the solids content of the sample is to simply dry a small weighed aliquot much as you dry each of the measured solution samples in the ALCA method A 20. For the concentrated liquor, though, a 100-ml portion would be too large and require too much drying time. Ten-ml aliquots of concentrated liquor were weighed and dried in order to determine solids content for the six liquors to be studied. After the required solutions were prepared the total solids was determined again in accordance with the requirements of method A 20, for comparison purposes.

Soluble solids/nontan determination

Soluble solids determination using the ALCA Standard Method requires folding filter papers and then conditioning them for one hour with constant recycling (collecting, uncovering, pouring back, recovering) of 225 ml of the dilute tannin solution, followed by an additional hour of collecting filtered solution from the kaolin coated filter paper. The exposed liquid and wet filter paper edges are prone to significant evaporation, especially in warm, dry conditions. Covering and protecting the filtering liquors is essential, though only partially effective, while adding significantly to the complexity and difficulty of the procedure. Conditioning the filter paper is done to saturate the paper with tannins so that, at least theoretically, none will be removed from the analyte solution, which is dumped into the filter after the conditioning solution is removed.

The filter paper and kaolin do not have to be conditioned for the non-tannin determination since removal of the tannins is a desired effect. Unfortunately, not conditioning the filter paper does not change the tedium of mixing kaolin, folding papers, recycling collected liquor, covering glass funnels and their wicking filter paper edges, and long collection times for the slow dripping solutions. As one old time journal writer put it, the tannin analysis method demands the full attention of one lab worker through the entire filtering process. After the analysis is complete, there is the matter of cleaning the 7 or more pieces of glassware dirtied for each sample and blank just in the non-tannin determination alone. Of course all these mechanical manipulations lend themselves to leaks, spills, contamination, losses and transfer (not to mention transcription) errors. In the end, if the data do not fall within the limits set for variability, or detectable failure occurs with a filter or transfer, the method simply prescribes repeating the entire process.

A review of current filtration technologies showed two promising products lines including syringe end filters and glass fiber membranes:

Syringe end filters were procured from the Pall Gellman Company. Upon company recommendation, two models of filters were selected, Acrodisk 4525 and 4559. Both offered glass fiber pre-filtration with a GHP polypropylene support ranging form 0.2 to 0.5 micron in pore size. These units were very difficult to force tan liquor through and clogged up after 3-5 ml of the first attempt at soluble solids filtration. Syringe end filters were then discarded as a filtering technique.

Glass fiber membrane filtration was attempted next. This was attempted using 47mm glass fiber membrane 61631, 66078 and 64798 from Pall Gellman in a Buchner funnel. Although very fast, (15-45-seconds/100ml sample) these filters did not leave the samples optically clear, as per ALCA method requirements. This method was also discarded.

Borrowing technology from other laboratory procedures was a third possibility. High Performance Liquid Chromatography (HPLC) requires very clean samples for analysis, to avoid clogging the column. Dr. Howard Jordi, Jordi & Associates, 4 Mill Street, Bellingham, MA 02019, was contacted to explore standard filtration methodologies that could apply for tannin analysis.

- Through development with Dr. Jordi, 60 mililiter extraction tubes were packed with 2g of diatomaceous earth, over a one-micron frit and evaluated. The initial test apparatus was a side arm flask with a rubber adapter to fit the extraction tube and an aspirator for vacuum supply. As the method showed similar results, on a very limited basis, to ALCA method, further study was indicated. All extraction tubes were supplied pre-packed with diatomaceous earth by Jordi & Associates. Extraction units were acquired to allow multiple concurrent extractions for time efficiency This allowed side by side comparison of ALCA method and extraction tube results.

- Early trials using extraction tubes showed very good repeatability and durability of tubes (10-12 extractions per tube before channelizing of celite). However, a second manufacturing run of extraction tubes showed a tendency to clog more quickly (3-4 extractions before blinding of filter). This effect was attributed to variability in two different lots of diatomaceous earth.

- Preparation of the extraction tubes requires flushing with distilled water several times under atmospheric pressure, followed by 2 X 60 ml volumes of water under (2-3"Hg) vacuum to remove fines. Optimal analytical results and filter longevity are achieved through extraction at minimum vacuum (3"-4"of Hg). Extraction tubes are flushed with ½" (about ten cc) of each consecutive solution before samples are gathered. Several soluble solids determinations are possible before the filters blind off or channelize. Vacuum must be increased with successive filtrations, as the filters start to clog.

- After a certain point the extraction tubes blind off, or channelize, necessitating replacement. Attempts to clean and reuse clogged filters showed mixed results, sometimes requiring extraction times surpassing that required by Standard Method analysis. Results generated by these extended extractions were also erratic. Although relatively expensive, at US $5.00 per tube, extraction for soluble solids and non-tans is very time efficient, at 5-10 minutes per set. The laboratory technician time savings (1-2 hours per set of samples) far outweigh the added cost of replacing clogged filters.

The modified procedure is:

1) Purge the extraction tube with 20 to 30 ml of the analyt-

ical solution being tested.
2) Fill extraction tube with solution.
3) Apply vacuum and catch filtrate in test vials in extraction unit.
4) Pipette filtered material into evaporating dish to evaporate.
5) Non-tans are defined as the residue left after analytical samples are shaken for 10 (ten) minutes with lightly chrome-tanned hide powder, filtered, and evaporated.

RESULTS

Total Solids

As shown in Table I the results of both methods of total solids analyses are very similar. A systematic difference in the values is apparent even though the numbers are virtually identical. This difference is related to the fact that the diluted solution prepared for the ALCA method is measured by volume while the concentrated liquor was simply weighed. If the density of the solution were unity (1.000) then the values would be identical, but the temperature (lowers density) and dissolved solids content (increases density) of the liquors have a combined affect which causes them to have a slightly increased total solids value. The ALCA Standard Method requires duplicate results to fall within 0.2% of each other for validity. Direct weighing of undiluted solutions gives results within 0.1% of the ALCA method. This leaves one to wonder "why do all the extra dilution and manipulation as well as risk handling errors, and handle extra glassware if it is avoidable?"

Soluble solids/nontans

Hermann Oak Leather Company is endeavoring to demonstrate the benefits of developing an adaptive attitude toward modernizing the tannery liquors test methods. Use of modern technology can: (1) improve the utility and ease of use of these methods, and (2) reduce the time and cost for analysis.

The focus of the early work has therefore been directed toward the most time consuming and difficult step in the test method for tannery liquors; i.e. the soluble solids and non-tannin solids determinations, which are laborious filtration procedures. This focus has resulted in:

- Eliminating the use of special filter paper.
- Eliminating the use of the complicated kaolin mixing and clearing steps.
- Creating the potential to shorten and simplify the analysis.
- Eliminating repeated handling of breakable glassware such as funnels, beakers and stirrers in cumbersome filter stands.
- Reducing the potential for injury.
- Reducing data errors.

TABLE I
Total Solids of Tanning Liquors by Direct Weight and ALCA Volume Measurement

Sample Number	Direct % Total Solids	ALCA % Total Solids
15	16.0	16.1
56	16.0	16.1
83	12.6	12.7
85	7.4	7.5
92	11.2	11.3
93	9.2	9.3

By substituting the plastic cartridge filters on a vacuum cell system with 12 collection ports for a 6 glass funnel gang, such as needed for ALCA paper filters and kaolin, hours of unsafe and difficult manipulations and waiting are reduced to minutes of simple pour and collect sample activity. An hour of filter conditioning can be replaced by a quick rinse and loading of the cartridge (cartridges do require pre-soaking to moisten the resin prior to use). Processing solutions of soluble solids and non-tannins solids can be transformed into simple operations of dumping solutions into the extraction tubes, collecting the filtrate, and pipetting the 100-ml sample to be dried. Preparation of nontan solution still involves shaking the tan liquor solution with prepared hide powder before addition of solution to filter. In soluble solids determination,the tan liquor solution is filtered directly.

Of course, the critical issue is whether the values obtained from the vacuum system are reasonably consistent with ALCA method values. Two sets of six tannery liquors were evaluated on a very casual basis in order to assess feasibility and similarity of outcomes. Preliminary results were very promising. A carefully collected battery of six liquors was then prepared and split between two analysts for a direct comparison of the two techniques. These samples represented a deliberate array of different vat liquor concentrations. Each sample was tested using ALCA method A 20 and two separate determinations at different laboratories with the vacuum system. The directly determined solids values for soluble solids and non-tannin solids are given in Table II. Soluble solids and non-tannins are the values actually determined in both methods. The insoluble solids and tannins are calculated values based on the total solids, soluble solids and non-tannins.

TABLE II
Comparison of ALCA Solids Values with Vacuum System Values

Sample Number	ALCA Method A20 % Soluble Solids	Operator 1 Vac. % Soluble Solids	Operator 2 Vac. % Soluble Solids
15	15.6	15.7	16.0
56	15.8	15.7	16.0
83	12.1	11.8	12.6
85	7.1	7.1	7.3
92	10.8	10.4	11.1
95	8.8	8.8	9.2
	% Non-Tannins	**% Non-Tannins**	**% Non-Tannins**
15	5.2	6.1	5.3
56	5.4	6.0	5.4
83	5.4	5.1	5.3
85	4.1	3.9	--
92	5.0	4.7	5.1
95	4.6	4.5	4.7

Clearly, all three analyses of these six tannery liquors produced similar values. Three different operators all performing the ALCA standard method would have likely gotten more divergent numbers doing the same determination, if indeed you could find three competent technicians who could or would perform the ALCA determination. Given the skill level required and difficulty in doing the ALCA standard method, these values are all the more impressive since the vacuum system operators are literally new technicians with very modest experience with such systems. Obviously a much larger sample would be required for a statistical evaluation of the variations within and between the data groups for the methods.

DISCUSSION

The possibility of tannin determination by direct methods has always held a strong attraction for laboratory personnel. Beyond the reduction in time consuming laborious procedures, there is less chance for data errors. The systemic difference between direct weight and volume determination must be considered when developing any new method. If direct weighing is used in any portion of the determination, then it must be used at all times.

In the hands of an inexperienced analyst, the errors and variations in the ALCA method (A 25) for determination of tannin concentrations are enormous. Even the seasoned analyst has to be constantly on guard to check and monitor each analysis. Few even try to meet the stringent limits set for hide powder checks (fat, ash and pH factors), blank values, (two with every set of samples that must have near zero outcomes), and concentration limits (maximum 3.5 grams tannin per liter for prepared solutions) dictated within the method itself. The ALCA method is difficult and tedious with a hard and extensive learning curve. Manual dexterity and speed are essential to avoid losses and maintain the sample integrity. Large supplies of glassware, ample space and climate controlled workspace are also important factors. Minor differences in hide powder, kaolin, filter paper, and other materials have been found to have real affects on analytical results. All of these factors mitigate against the practical application of the standard ALCA method for tannery liquor analysis. Now add the uncertainty and cost of supply for any hide powder, specified filter paper and unique kaolin, and you have untenable complications in use of the method.

The crucial experiment in this effort involved the soluble solids and non-tans determination. The primary point being that the method (A 25), as written, requires several days to complete. This method requires preparing solutions and hide powder that must stand overnight, then pre-conditioning filters and filtering, and finally drying 100 ml aliquots of the filtered liquids overnight. This process requires careful planning and execution so that glassware, filters and solutions are ready at the critical times with adequate time to complete lengthy procedures in the time frames allowed, i.e., within a reasonable work day. The cost of having outside laboratory analysis is increasingly prohibitive with modern wages and overhead costs. These factors of procedural difficulty, material procurement, and cost dictate that the method must be improved or replaced if it is to survive in any kind of usable and meaningful form. Simply ignoring the development and improvement of the method to fit current needs, as has been the case since 1954, only ensures its eventual demise.

By contrast, the new vacuum cartridge technique is fast, simple, much less susceptible to evaporative losses, leaks, spills, filter tears, equilibrium disturbances (kaolin disturbance), and transcription mistakes (samples transferred through many vessels in amongst many other samples under going similar transfers). Anyone can learn to do it quickly and easily since it is almost as direct as pouring through a filter, collecting the filtrate and measuring off the desired sample for drying. Several hours of difficult filter folding, conditioning, monitoring and cleaning are reduced to a few minutes. All the cartridge filters, vacuum cells, vacuum pumps and other materials are readily available and reasonably inexpensive. Glassware use with the attendant costs, safety issues and storage problems are reduced.

Conclusions

The intrinsic difference between direct mass and volume determination of analytical values must be considered for any new method developed for tannin analysis. It is crucial that all determinations in any new methods are compatible in the basis for calculation.

Simple cartridge filters attached to a vacuum cell can simplify and dramatically shorten the analytical work and time for ALCA tannery liquor analyses, yet give results similar to the Standard Method.

Future Research

Pre-filtering to extend the life of cartridges and to lower cost will be evaluated. Further trials using combinations of filtering technologies will be explored. Eventual transition to chemical characterization through direct analysis will be pursued to quantify and identify active tannin content of liquors and raw materials.

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Convention Discussion

William Marmer, ERRC, USDA - I was wondering whether you tried to centrifuge the samples to try to clarify them?

No. Actually, that would be a good idea to try. That would obviously end up with a optically clear sample. I think that is something that we should look at in the future. The downside is that centrifuges, in general, generate fairly small samples. We are required by the method to run 100 ml samples. Short of getting a very large centrifuge, it would take quite a few tubes to end up running out 100 mls of it. However, it would be a good idea to evaluate in the future.