XI. ON THE COMPARATIVE VALUE OF THE SEVERAL METHODS OF DETERMINING TANNIC ACID.

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This investigation was to determine the relative accuracy of the following methods: Lœwenthal's latest modifications of his old method; Hammel's skin and specific gravity process; Carpené's indigo method as modified by Barbieri; the old gelatin process, highly refined; Allen's lead method, as modified by Sanford, and my own method, a modification of Lœwenthal's.

In the first place, I would like to state that every evidence that I can bring to bear shows that there is but one tannic acid—a principle which has the peculiar property of combining in the proportion of 10 parts by weight with 6 parts by weight of skin to form leather. In nature this principle is often mixed with glucosides, so-called extractive matter, etc., and hence the various formulæ assigned to what have been supposed to be different tannic acids. I propose to show proof of this in a subsequent paper. Where tannic acid is mentioned in this paper the above principle is meant. It can readily be obtained pure from nut galls and oak and hemlock bark. When obtained from kino and catechu (the so-called catechu tannin) it is accompanied by an extractive principle which renders the tannate of copper soluble in ammonia.

For the purpose of standardizing the numerous solutions to be used, an absolutely pure tannic acid was examined. Its preparation was conducted thus: A fair quantity of coarsely ground Aleppo nutgalls was taken and treated with ether and water, after the method of the U. S. P.

The product thus obtained was then thoroughly washed with absolute alcohol, dissolved in absolutely pure ether, and this repeatedly agitated with water until all of the tannic acid was thought to be extracted from the tannin; it was then separated from the ether by evaporation finally in a vacuum; was then dissolved in 80 % alcohol, filtered and separated from this as above; this well dried over sulphuric acid, and at a gentle heat in the air bath in a current of pure, dry carbon dioxide; a portion of it was burnt, and twice yielded a proper formula.

A solution of this was prepared containing 2 grams to a litre;

this solution was kept in a colored bottle out of contact with the air by carbon dioxide, and when not in use, for greater precaution, the bottles were placed in the dark. No change however occurred in their relation to the permanganate solution.

Pure gallic acid was prepared from nut galls. It was carefully recrystallized and readily obtained pure.

A solution of this was prepared as of the acid and was carefully kept.

Pure English gelatine (Nelson's), was used after purification, and a solution of it was prepared immediately before use by dissolving 25 grams in a litre of a 10% solution of sodium chloride.

The permanganate of potassium solution contained 1.5 grams to a litre, and was frequently renewed during the investigations, the acetate of lead solution for Allen's method contained a deci-nomal quantity of the pure acetate of lead.

The indigo carmine solution was prepared by dissolving 3 grams of the pure preparation in a litre of water. It was boiled for some time and carefully kept; did not change its relation to the permanganate solution a fraction of a cubic millimetre. The other solutions were all prepared as required with every care and precaution.

For the objects of the determinations, decoctions were prepared of hemlock, oak and chestnut barks, Aleppo nut galls, sumach leaves, and of the so-called catechu, tannins of catechu, kino and rhatany root. As they were all prepared and kept under the same conditions, I will only detail the mode of extraction of the first and most important one, hemlock. To a litre of the decoction in view 20 grams of the coarsely ground select inner bark of the hemlock was taken; this was extracted by carefully heating it with water in a current of carbon dioxide, allowing the decoction thus formed to cool, and then filtering it through four thicknesses of filtering paper; a very small amount of dilute sulphuric acid was then added to the solution and it was again filtered, the excess of acid neutralized by baryta water and filtered. The decoction was thus freed from the so-called extractive matter and contained tannic and gallic acids nearly pure. This decoction was preserved in an atmosphere of carbon dioxide. The decoctions of catechu, etc., were prepared and kept in a similar manner but still retained a strong color; they are, I may add, much less liable to change, owing to the peculiar principles present. Tannic acid prepared from these solutions by a process similar to the one used for galls, had a variable constitution, differing materially from that of the pure tannic acid obtained from the others.

I will first consider Lœwenthal's method (Fres Zeitschr. 1877, pp. 33 and 201.) This method has been highly commended by Proctor and others, but in working with it I soon found that it gave results at variance with practical experience and with my control method as will be detailed later. Portions of each of the ten different decoctions were taken and the analysis conducted in strict accordance with Lœwenthal's directions. Thus : 20 cc. of the indigo solution was first titrated. It required exactly 8.4 cc. of permanganate solution. The titrations were conducted in a porcelain dish; ¾ of a litre of solution and 10 cc. of dilute sulphuric acid were used in every case. 10 cc. of the standard tannin solution, with 20 cc. indigo solution and acid as above, required 13.7 cc. Deducting 8.4 cc. for the indigo we have 5.3 cc. used, for the tannin.

This same operation was repeated, using the decoction instead of the standard solution. 15 3 cc. were now used, or 6.9 cc. for the decoction.

100 cc. of the decoction were then taken, placed in a flask with 50 cc. of the gelatine solution and 100 cc. of a saturated sodium chlorride solution, containing also 25 cc. of sulphuric acid and 50 cc. of hydrochloric acid per litre. Between the additions the mixture was well agitated. It was allowed to stand over night, and a perfectly clear filtrate taken off the next morning. To save calculation 25 cc. of this, equaling 10 cc. of the undiluted decoction, were taken and tested as above, using 11.45 cc. of permanganate, or 3.05 cc. for the impurites, etc., not tannic acid. Subtracting this from the figure 6.9 cc. leaves 3.85 cc. and we have the equation;

5.3 : 3.85 = 0,2 grms. to a litre : x grms. to a litre. x = 1.45 grms. to 20 grms. of bark, or 7.25 per cent., the value of the bark. This, as I will show beyond, is lower than is really the case. The figures obtained were:

No.	20 G Hemlock.	20 G Oak.	20 G Chestnut.	15 G N. Galls.	10 G Sumach.	10 G 5 Catechu.	2.5 G Kino.	3 G Rhatany.
1	7.25	7.40	6.00	52.5	13.5	47.0	82.0	About 80.00
2	7.00	7.30	6.00	56.3	12.9	51.0	82.0	
3	7.30	7.45	6.10	54.2	12.9	48.0	82.0	
4	7.20	7.25	5.90	55.0	13.3	49.0	82.5	
5	7.25	7.00	6.30	55.5	13.1	48.0	81.3	
6	7.20	7.00	6.00	53.0	12.8	50.0	83.0	
7	6.9	7.16	5.90	55.6	13.2	51.0	82.0	
8	7.25	7.30	6.20	54.4	13.25	49.0	82.0	
9	7.10	7.20	6.00	54.5	12.95	50.0	83.0	
10	7.15	7.10	6.15	52.8	13.2	48.0	81.5	
Average.	7.16	7.21	6.15	54.4	13.1	49.0	82.1	
Real Value.	7.90	8.22	7.42	61.5	16.25	40.0	72.0	34.00

giving altogether an average value about 95 out of exactly 100 per cent. But as this is an average including the discordantly high and low it is not to be wondered at. The value however for the first five is about 86 per cent. and for the last two 117 per cent.

The errors are incurred because the tannate of gelatine is more or less soluble in a weak gelatine solution even when chloride of sodium or the strong acids are present; in fact although the acids facilitate coagulation they also dissolve a portion of it. It is also somewhat soluble in solutions of gallic acid as is shown by the figures in the nut gall column of the table; moreover much gelatine remains in the solution The quantity is very variable as it depends upon the amount of so-called extractive matter present. As I will show further on all those errors together produce an effect —amount to perhaps 40 per cent. This is, however, partly complicated by the amount of oxidizable matter and gallic acid which are also, when together, precipitated partly with the tannate of gelatine by the withdrawal of the tannic acid which holds them in solution. This is shown in the column under rhatany where so much matter depending on the tannic acid for its solution was precipitated as to render even approximation impossible. It is also shown in catechu and kino but to a less extent; this is what some in good faith call tannic acid, and ascribe to it a formula. They probably never combined an ounce of tannin with skin in all their lives, so their ignorance is pardonable. In the last three determinations, I used as near as possible the exact amount of gelatine necessary and a minimum of acid solution, with but little difference in the results.

This method surely is a very satisfactory one as far as it goes, as it is very easy to execute and has not so many of the difficulties peculiar to some of the others; it however, does not come up to my requirements. The value of this method, especially its use in determining the values of spent liquors was investigated. These liquors contain many unknown principles derived from the skins in their treatment,and thus their accurate determination is very difficult. This and another method of determination are the only ones that can be used at all. It is of great importance to the tanner to know how his spent liquors and the spent barks run in strength. The spent liquors were taken, treated with sulphuric acid, etc., as above, and the determination proceeded with. Five analyses were made of the spent liquors direct from the vats after a run with Buenos Ayres skins well cleaned and raised—oak and hemlock liquors and those from catechu were also taken. They had been used on fine skins but were good samples. The results are stated in absolute per cents.

No.	Oak.	Hemlock.	Sumach.	Catechu.
1	.13 per cent	.08 per cent	2.95 per cent	2.90 per cent
2	.14 per cent	.085 per cent	2.90 per cent	2.93 per cent
3	.125 per cent	.08 per cent	2.95 per cent	2.93 per cent
4	.16 per cent	.08 per cent	2.93 per cent	2.89 per cent
5	.145 per cent	.085 per cent	2.90 per cent	2.90 per cent
Aver.	.140 per cent	.0825 per cent	2.93 per cent	2.91 per cent
Real value	.27 per cent	.21 per cent	1.62 per cent	1.90 per cent

These figures are, of course, only approximate, but are quite exact proportionally. The causes of such great errors are these: Much less matter is separated with the tannate of gelatine, a very large proportion in fact, nearly all of the latter dissolves and the amount of gelatin left in solution is very considerable, so that there is merely a perceptible difference in each two determinations. With spent barks there is but little difference from the result noticed above, they being a little higher by compensation.

Now the prime argument. To show the misleading results given by this method and to show the control used, we will consider hemlock bark No. 1 analysis all through: Here in the first table we find it to contain 7.25 per cent, of tannic acid. We take a cord of this bark, leach it, and obtain 1,250 gallons of decoction. The spent bark is analyzed by this method, and found to contain .7 per cent. of tannic acid. Leather is tanned from the decoction with great precaution, and what is 5 per cent. of the bark found to have been used. As I will show further on, this was pure tannic acid. The spent liquor is also examined, and found to hold what was equivalent to 5 per cent. of the bark in tannic acid. That is to say, the same—as we would speak of the spent liquors as containing nearly all the tannin of the bark, or 6.5 or 7 per cent. of it, in tannic acid. However, all these figures added together give a result of 6.2 per cent., or 1 per cent. unaccounted for, thus showing the result to be too low. The tannic acid had not decomposed, as I used a preservative to keep it, and one which I know to be thorough and complete.

Now, if the spent liquors be examined by say the method I will note further on, we find it to contain just twice as much, or 1.4 per cent. This would bring it up to 6.9 per cent.; still too low; but by examining the spent bark in the same process we have 1.5, instead of 5, and the figure is brought up to its nominal value then proved of 7.9 per cent.

According to the reasoning deduced from this process, we would have 6 per cent. of the bark utilized as tannin to combine with the leather Nothing is more erroneous than this, as is proved every day by the tanner; as never over 5 per cent. is obtained from hemlock, the others in close proportion. So much for this process.

Next in order of our consideration comes Hammond's method, and its modifications, which were so popular some time ago; among some of the tanners the results obtained by it were so inaccurate and inconsistent as to speedily set it aside. The many inaccuracies have been partially shown by a number of investigators, especially Proctor, who has shown that gallic acid is thrown down with the tannin, etc. The method was as carefully tested and examined as the other, and the results are here tabulated :

No.	Hemlock.	Oak.	Chestnut.	Nut Galls.	Sumach.	
1	10.2	13.2	10.0	34.0	10.00	Catechu, Kino, and Rhatany, not accordant results.
2	6.5	6.4	4.8	43.0	11.00	
3	9.9	9.3	9.2	56.0	6.5	
4	11.4	12.4	7.4	40.0	7.6	
5	9.6	14.0	6.9	61.0	9.8	
6	6.8	4.0	11.2	52.0	6.9	
7	11.2	8.0	10.2	57.0	8.2	
8	6.9	12.5	4.9	49.5	7.4	
9	8.4	5.0	8.6	45.0	10.5	
10	10.5	10.0	9.4	56.0	6,8	
Average,	9.14	9.48	8 26	49.0	8.57	
Real value,	7.90	8.22	7.42	61.5	16.25	

These figures were obtained in the following manner The decoctions, filtered and treated as before, were placed in a graduated jar, and the specific gravity taken by the use of a very delicate densimeter. The skin was then taken, thoroughly cleansed, heated and raised by appropriate treatment. It was then thoroughly washed with a solution of gallic acid, again with acetic acid and warm water, until it was pure and sweet. It was then placed in water with the decoction, and allowed to air for an indefinite period, for the first five analyses. It was then taken out and scrubbed off as far as possible without altering the bulk of the solution, the specific gravity of which was then taken. The amount of tannic acid was calculated from the difference, etc.

The details of the method were executed with much more refinement than is the case generally, and the principles involved thoroughly worked out. But with this look at the result one might reason, Why would not the result be identical with the practical manufacture of the leather, or 5 per cent, etc? This I can readily show. In the first place, to obtain the decoction for their determination, or rather to make solutions uniting all the tannin in the material used, we have to extract much more extraneous matter, especially in the case of rhatany, kino and catechu, than in the imperfect leaching of the tanneries, where in the case of the last materials only 50 per cent. of the tannin present, and a minimum of coloring matter, are extracted; thus the the leather has less to contaminate it. In the second place the sample of skin is never a fair specimen in the treatment of a whole hide, and besides, the leather formed cannot be properly freed from the different matters besides tannic acid soaked into it, without altering the volume of the solution. It must be remembered that leather after it is formed is thoroughly rolled, and scrubbed so as to leave nothing but leather. The leather absorbs tannic acid and the so-called extractive matters; and by withdrawing the tannic and partly the gallic acid from a solution much matter is deposited, partly in the solution, some in the leather. This by the above treatment is removed before the leather is dried and weighed; thus much matter is abstracted and accounted for as tannic acid, this yielding too high results. Besides these considerations the densimeter must have extreme delicacy, and even then a small space on the scale represents much tannin. Altogether, I pronounce this method little better than a guess; in fact a tanner can arrive at the strength of his liquors by their taste better than by this method.

In the examination of spent liquors and barks this method was of no value at all, as it gives such very inconsistent results. This is caused by the putrescent matters present in the liquor and other causes. In the spent liquor the analyses turn out like those shown in the table below :

No.	Oak.	Hemlock.	Sumach.	Catechu.
1	6.5	4.0	7.9	4.0
2	2.2	5.2	8.4	3.0
Average,	4.3	4.8	8.2	3.5
Real value,	.27	.21	1.62	1.90

In fact, Hammer's whole method, however modified, is the same thing. This instrument should be done away with in the tanneries as it only shows how much matter, tannic and otherwise, especially otherwise, *is in solution.*

In the use of this method and the worthless modification of drying the skin filterings and weighing before and after treatment, chemists and others generally obtain the results too low, but that depends on the very nice point of understanding how to make leather.

Using the calculations applied to Lœwenthal's process for a control we find thus: In No. 1 the leather 5 per cent., the spent liquor 3.5 per cent., the spent bark 4.5, all together 13 per cent. This is quite far from the average value of the bark, which will be noticed was 9.48. Giving the proper value to the spent liquor (1.4 per cent.) the result is 10.9, or much nearer the truth.