

XIV. ON THE COMPARATIVE VALUE OF THE SEVERAL METHODS OF DETERMINING TANNIC ACID.—PART 2.

BY NELSON H. DARTON.

The next method examined was that of Carpené, as improved and modified by Barbieri. This method was looked forward to as an excellent one when first proposed, and consequently was brought into use almost immediately. The details of the execution were very simple, and its originators obtained excellent results. Some time after, Kathreiner examined into its value, and stated* that with it he had only been able to obtain exceedingly inaccurate and discordant results, and had failed in his endeavor to favorably modify it. In his investigations he employed a decoction of sumach and a solution of the so-called "pure tannin" of the shops, and thus the comparison between the sumach and this compound, containing not over 80 per cent. of digallic acid, was not a correct one. The other 20 per cent. of the so-called "tannin" was composed, as I have found, of matter nearly all precipitable by ammonia solution, and the importance of taking this into consideration is shown below. Thus the poor results obtained by Kathreiner are explained. I have, in the investigation of this subject, applied this method to most of the other tanning materials, and have in this manner brought some new facts in relation to it to light, not only by employing the variety of the substances tested, but also by varying the conditions of procedure and investigating the source of the errors. My general mode of procedure was as follows: Using as before, for example, the decoction of hemlock bark, though not in strict accordance with the details as published by Bolley in his *Handbuch*, but with as much modification as experience had shown to be desirable. The decoction was taken in convenient quantity, an excess of a solution of ammonia added to it, and the precipitate thus produced filtered out. A known amount, which was also an excess of a solution of ammonio-acetate of zinc was then added, and the bulk of the mixture brought up to a given point by the addition of sufficient water; the precipitate formed was allowed to separate as far as possible by standing, and the mixture then boiled down at a low heat in a partial vacuum to half (or to any specified degree) of its original volume. After allowing it to cool thoroughly the

* Dingler's Polyt. Journal 227, p. 481.

precipitate was filtered out and washed as completely as possible with a known volume of water heated to about 80° C.; it was then dissolved in warm diluted sulphuric acid, titrated with the permanganate of potassium in presence of indigo-carmin, and

No.	Hemlock.	Oak.	Chestnut.	Nut Galls.	Sumach.	
1	9.30	10.00	5.50	67.00	10.00	Catechu,
2	12.00	12.50	6.50	69.00	13.50	Kino
3	10.00	9.50	5.20	65.50	11.00	and
4	11.00	11.20	7.00	68.20	13.00	Rhatany,
5	8.50	9.00	6.00	60.00	9.00	
6	18.60	13.00	9.00	69.00	19.00	non-
7	11.00	12.00	6.00	66.00	11.00	accordant
8	20.30	15.00	11.00	72.00	20.00	results.
9	8.50	7.50	6.20	60.00	14.50	
10	3.00	5.20	2.80	47.50	3.50	
Average.	12.20	10.40	6.50	62.40	12.50	
Real value.	7.90	8.22	7.42	61.50	16.25	

and the result calculated from the data so obtained as in Lowenthal's method. Above is a table of the results obtained, in percentages. The great differences which it will be noticed, occur so abruptly are principally caused by varying the conditions, and I will detail them individually. Result number one was obtained by having the amount of zinc solution, in excess, a minimum, and conducting the evaporation in the shortest possible time. Number two was obtained by omitting the preliminary ammonia treatment preceding the addition of the ammonio-zinc solution, and in exact accordance with the detail of the method as originally proposed and published in *Bolley's Handbuch*. It is the treatment with the ammonia that causes the great difference in these two results, as a fair amount of precipitate was in that way separated which would otherwise have been precipitated with the tannate of zinc by the ammonia then added. Result number three was obtained by titrating the solution before and after the separation of the tannic acid by the zinc under the same condition as in number one, thus the method was modified to the principle involved in Lowenthal's. Result number four was obtained in the same manner, except with the omission of the ammonia treatment. Notice the difference in the result. Returning now to the original mode, in number five the evaporation of the mixture was to only two-thirds of its volume, and in number six to one-third; numbers seven and eight were

respectively conducted under the same conditions as numbers five and six omitting the preliminary ammonia treatment. Two blank samples of decoction were taken in this connection and evaporated down to one-third of their original volume, one after the preliminary treatment with ammonia the other omitting it. In both cases considerable matter deposited, although more in the latter than in the former, thus showing how numbers six and eight have been influenced. Result number nine was obtained by using almost the exact amount of zinc solution necessary, evaporating at a very moderate rate down to two-thirds, and with the preliminary ammonia treatment. Number ten was obtained by just the reverse of number nine, with the exception that the evaporation, although very rapid, was down to the same point. All the figures together have a value of 85% : result number nine a value of about 82%, higher by far than any single one of the other results, but still too low for accuracy, as a confirmatory duplicate of this result yielded a value differing by 10% at least. The causes of the discrepancies are these: The compound formed with the zinc is quite soluble in an excess of zinc solution; this was ascertained by several trials. Besides this error, which in number ten is shown to be considerable, in the concentration of the mixture other matter precipitates mixed with the zinc compound besides that which would be thrown down by the preliminary ammonia treatment, although I have found that the matter which has the tendency to precipitate when the tannic acid, its solvent, is abstracted from the solution, is held in solution by the free ammonia present, and thus in this and my own method that source of error is not introduced to the slightest extent, while, as I showed before, it so markedly influences the results of Hammel's and Lœwenthal's method. In boiling the mixture down at too high a heat the ammonia is evolved and this matter besides the gallate of zinc, etc. precipitates for want of the solvent. This is well shown by the lower result of number nine, which, as I before noticed, was evaporated more slowly than number one.

Take this method and modify it by the preliminary treatment with ammonia and filtration, which is shown by the above reasoning to be of such importance, use little or no excess of ammonio-zinc solution, by finding the quantity necessary by a preliminary treatment, evaporate the mixture down by one-third of the original volume at a moderate rate, and thus results similar to number nine may be obtained. I will notice here that the tannate of zinc formed in this process, as well as the tannate of copper, as I have shown in a pre-

vious paper, are quite free from extraneous matter when from the oak, hemlock, galls, etc., but from the catechu, kino, etc., are very markedly contaminated, and thus the notice in the last column. As the examinations in this line were not continued, on ascertaining the first few results, with spent barks and liquors this method yielded too unsatisfactory results to be used at all and thus I am unable to tabulate my conclusions as I did of Lœwenthal's and Hammel's methods, but I might add that it compares favorably with either in all its relations.

The next method examined is the gravimetric gelatin method, which is objectionable as not being a volumetric one. When first proposed by Sir Humphrey Davy this method was much used, and is in fact up to this day in more or less constant use in the primitive condition; but after Watts published his researches upon the numerous inaccuracies, showing that the tannate of gelatin was exceedingly soluble in an excess of its precipitant, taken together with the difficulty encountered in filtering it off, owing to its slimy nature, it lost favor, and was seldom used by scientists. Some time ago Stoddart showed that by adding alum to the solution, both of these difficulties might be avoided to a great extent and fair results obtained, although if not of the absolute amount of tannic acid present, between this and the amount available for the formation of leather. But taken under any condition, this method, as I will show, cannot be compared with Hammel's, or much less Lœwenthal's. In the examination of the method a series of five determinations each were made, and the results shown by the table below in percentages. All the causes of these grave errors, excepting the one I will notice below, are of the same character as those I detailed under Hammel's method, but without the introduction of extraneous matter, as when using hide. They have acted to a much more limited extent in this method, however, and thus the difference in the results.

No.	Hemlock.	Oak.	Chestnut.	Nut Galls.	Sumach.	
1.	5.30	6.20	3.50	50.20	10.00	Kino,
2.	4.20	3.80	3.60	52.00	13.00	Catechu and
3.	6.00	5.50	4.90	54.00	11.00	Rhatany, non-
4.	3.70	4.50	6.40	51.50	9.50	accordant re-
5.	4.50	4.30	5.30	56.00	14.00	sults.
Average,	4.70	4.80	4.70	52.90	11.50	
Real value,	7.90	8.22	7.42	61.50	16.25	

Owing to the influence of a cause comparatively absent in Hammel's method, the results are not solely affected by these inaccura-

cies. This cause is the solubility of tannate of gelatin, even in presence of the acids of Lœwenthal's method, though a little less there if alum has acted to such a degree as to make the results as low as some of the lower ones of Hammel's method.

Besides this, it may be well to recall to your attention here, that a solution of gallic acid is a powerful solvent, and especially in relation to this precipitate. The figures for the table were obtained in the following manner: The decoction was taken in measured quantity, mixed with sufficient alum solution and filtered from the resulting slight precipitate. A trial precipitation was first made to ascertain the approximate quantity of gelatin solution necessary, and then to another portion the necessary amount was added. The mixture, after a violent agitation, is set aside over night, and upon the next morning the precipitate is filtered off and washed with sufficient water at 5°C. After draining over the pump it is dried at 90°C. and weighed in the filter paper, the weight of which is known. The results in the table show this method to yield entirely too variable, and at the same time low figures, and therefore that the method cannot be employed in any determination where accuracy and speed are sought. The table shows a value of 87 %, I may add, but varies from this to 30 %. With "spent liquors" and "barks" the results are still more erroneous. Below are five determinations of the value of "spent liquors" in percentages of their weight:

No.	Hemlock.	Oak.	Sumach.	Catechu.
1	Hardly determinable.	0.10	.90	.50
2	" "	0.10	.40	.60
3	" "	0.10	.70	.50
4	" "	0.10	.50	.70
5	" "	0.10	.60	.60
Average,		0.10	.62	.60
Real value,	0.21	0.27	1.62	1.90

These figures do not afford me the necessary data to reason from in relation to the control, which is in this method thus unattainable.

The next method examined was the volumetric modification of the above. This method, which is even in use at this time, is nearly as inaccurate, and although a volumetric method, even as tedious as the other. The principal difficulty in the execution, and also in the accuracy of this method, is distinguishing the point at which there is no excess of either gelatin or tannic acid. This is literally impossible, as in the titration we encounter a condition in which

either the one or the other will produce a marked opalescence, and this lasts until a cubic centimetre of the one has been added in excess. This in itself condemns the method, besides there are the same inaccuracies which influence the results of the first and last method discussed. Another thing to be considered in both this and the preceding methods is, that tannic acid combines with a proportion of gelatin depending upon the amount of tannic acid present, or rather remaining in solution. To express it simply, the first portion of tannate of gelatin precipitating contains a much greater proportion of tannic acid than that falling when the quantity of the latter has decreased. Thus very variable amounts of the titrating solution may be used under varying degrees of dilution, and less or greater additions of it. In obtaining the results shown below in the table, the volumes of the standardizing solutions and those under examination were kept equal, as was also their approximate strength. The gelatin solution was added in c. c.'s at a time, and thus similar conditions existed as far as possible. The first five results were obtained from comparison with a standard solution of tannic acid, containing one gramme to a litre, and the others with the regular solution prescribed before for the other determinations. The mode of procedure was essentially as follows: The decoction in convenient quantity was placed in a beaker standing upon a blackened plate, and the gelatin solution added from the burette in c.c.'s at a time, at first at intervals of ten minutes, then of twenty minutes, and finally of one hour; when the end reaction was approximately found by taking out drops on a glass plate placed over some black glazed paper:

No.	Hemlock.	Oak.	Chestnut.	Sumach.	Nut Galls.	Catechu.
1	3.50	4.00	3.50	10.00	49.00	25.00
2	7.50	6.00	3.90	8.00	54.00	31.00
3	6.20	3.40	6.20	11.00	57.00	17.50
4	4.00	5.50	4.50	9.50	51.00	32.20
5	5.00	4.50	5.50	3.00	53.00	35.00
6	6.40	7.10	4.60	11.00	52.00	29.00
7	4.20	5.50	5.40	13.00	56.00	34.00
8	3.90	6.30	6.40	9.50	53.00	33.00
9	4.70	4.20	3.80	11.20	51.90	34.50
10	5.20	7.30	4.70	11.60	54.00	31.50
Average	5.10	5.43	4.85	10.78	53.20	30.27
Real value.	7.90	8.22	7.42	16.25	61.50	40.00

The average value thus deduced is 84 per cent., a little less than that of the others, but the figures are so discordant they condemn the method as little more than a mere surmise. In the determination of the strength of "spent barks" and "liquors" the results obtained are even of less value, as the following table will show: Numbers in percentage:

No.	Hemlock.	Oak.	Sumach.	Catechu.
1	trace	.15	.90	.80
2	.10	.20	.50	.90
3	trace	trace	.70	.80
4	.10	.10	.90	.70
5	.15	.15	.80	.90
Average,	.07	.12	.76	.82
Real value,	.21	.27	1.62	1.90

These figures were obtained as in the first five in the preceding table.

The next method examined was that of A. H. Allen, or rather Stoddart's modification of it. In the examination of this method the first five series of results were obtained by using swollen gelatine to separate the tannic acid, and in the last five by using a piece of hide properly cleansed, bated and raised. The general mode of procedure was as follows: A convenient amount of the decoction is measured out, and the standard solution of acetate of lead added, until a drop of the mixture filtered off ceases to color a mixture of ferricyanide of potassium and solution of ammonia with the characteristic red tint peculiar to the presence of, or in this case the excess of, tannic acid. Another portion of the decoction is then taken and the tannic acid separated from it as far as possible by the hide or swollen gelatin, as the case may be, and the remainder titrated as before. If the method was as accurate as might be supposed, no tannic acid would remain in the solution after this treatment, to afford the end reaction necessary in this titration, but as sufficient tannic acid does remain the end reaction is readily found. If the absorption of the tannic acid by the hide or gelatin was not so extremely tedious, and the errors noticed under Hammel's method more or less introduced, this method would rank far above Lœwenthal's, as the end reaction is perfectly perceptible when only $\frac{1}{1000}$ part of tannic acid is present; and besides this, it is somewhat unsatisfactory to be necessitated to filter off small portions continually for observing the end

reaction. The results shown in the table below are very fair, but too high in the first five; and altogether unsatisfactory in the others.

Number.	Hemlock.	Oak.	Chestnut.	Nut Galls.	Sumach.	Catechu.	Kino.	Rhatany.
1	9.50	10.00	9.00	69.00	19.50	47.00	82.00	86.50
2	9.50	10.00	9.50	68.00	21.40	44.00	76.00	89.00
3	9.80	10.00	8.50	69.00	74.00
4	9.60	11.00	10.00	67.00
5	9.40	10.50	9.00	67.50
6	7.10	6.50	11.00	52.00	14.30	51.00	64.00	42.00
7	11.60	9.30	6.00	67.00	21.00	38.00	29.50
8	12.60	6.90	4.30	49.90	19.00
9	6.40	8.40	9.20	57.00
10	9.20	11.10	7.00	67.50
Average,	9.37	9.37	8.35	63.30	19.10	45.00	74.00	87.00
Real value,	7.90	8.22	7.42	61.50	16.25	40.00	72.00	84.00

The value deduced from these figures is about 90 %. With "spent liquors" and "barks" the results obtained are even more fluctuating. Below is a table of a few determinations of "spent liquors";

No.	Hemlock.	Oak.	Sumach.	Catechu
1	1.50	2.00	4.00	3.50
2	1.50	2.50	4.50	3.50
3	2.00	2.00	3.75	3.50
4	1.25	2.00	4.00
5	2.00	2.25	4.00
Average,	1.65	2.15	4.50	3.50
Real value,	0.21	0.27	1.62	1.90

in these the tannic acid was separated by gelatin, and these although more at variance with the truth than the others, are of some slight value when compared with Hammel's method. If in this method the tannic acid could be separated by some more appropriate process, it would yield even better results than any other now known. The next methods examined were those of Clarke and of Jean. The first is an ingenious method, using, as we know, a standard solution of cinchonia sulphate and magenta for an indicator, although yielding extremely poor results as at present executed. In fact, I saw almost immediately that nothing could be learned by examining it further than to justify these remarks. I believe that it is capable of favorable modification, and I will attempt to do this if possible. Of the last, Jean's, I can say but little; it, as some may know, consists of titrating with iodine, using starch as an indicator. The results obtained in a few preliminary

examinations were sufficient to discourage further investigation. It did not yield a value of over 60 per cent. Besides an error in the principle involved, an error is present similar to the principal one in Allen's method, that is, in the separation of the tannic acid by hide, etc., between the titrations of which six at least are necessary, even after the solutions are standardized (which also requires six), the first two for the approximate value, and the four others for the two final determinations.

To Mettenzway and Terriel we are indebted for the most ingenious as well as purely scientific method of determination, and one yielding far more accurate results than any which Proctor has examined. The method, I may add, consists in the deduction of the amount of tannic acid present by the amount of oxygen it is capable of utilizing to become oxidized. This method, however, has the insuperable disadvantage connected with it of having a very difficult mode of procedure, and is only successful under the careful manipulation of experienced hands, thus rendering it impossible except under special circumstances. Some time ago, but not in view of these investigations, I examined into its accuracy and formed these conclusions. In time I propose to modify this method if possible, to render it more simple in detail.

The next and last method examined was that of my own modification of Löwenthal's and of Fleck's methods which I proposed some time ago before this society. I have given this method a most thorough and prolonged series of examinations, carefully controlling the results with working tests on a large scale. As it would take up too much space to detail the entire result of my investigations upon this method, I will only give a portion of them fairly and impartially selected, and at the same time from those executed under the the same conditions as were the preceding examinations. I will not detail my mode of procedure, as I have discussed it before the society at previous meetings, but I will here remark that the preliminary treatment of the decoction with diluted sulphuric acid is absolutely necessary, as the ellagic acid thus separated would otherwise interfere seriously with the copper precipitation, and would also call attention to the necessity of a preliminary ammonia treatment and filtration as in Carpené's method. In relation to the titration the suggestion of Proctor is available here. He suggests that the titration be conducted in a white porcelain dish and the first occurrence of the red or pink tint be noted, rather than

the yellow which is looked for when the titration is conducted in a flask. This red or pink tint is formed by the addition of one drop of the permanganate solution in excess and is observed around the edge of the apparently colorless space, where the depth of the solution is slight, next to the porcelain on the sides of the dish. I also wish to call attention to the necessity of using twice as much permanganate for the solution of indigo carmine alone, as is necessary for the tannic acid, etc. In the solution or decoction, as the case may be, I prefer to obtain my figure-not by comparison with oxalic acid but under corresponding conditions with absolutely pure tannic acid.

No.	Hemlock.	Oak.	Chestnut.	Nut Galls.	Sumach.	Kino.	Catechu.	Rhatany.
1	7.80	8.10	7.50	59.50	17.00	86.00	45.00	57.00
2	7.85	8.10	7.50	59.00	16.50	84.00	45.00	55.50
3	7.75	8.15	7.50	58.50	16.90	86.00	45.00	58.00
4	7.95	8.25	7.45	59.00	16.75	85.00	45.00	57.00
5	8.05	8.20	7.50	59.00	16.40	86.00	45.00	59.00
6	7.85	8.10	7.40	59.00	15.95	84.00	44.50	56.00
7	7.80	8.30	7.35	60.00	16.20	85.00	46.00	56.50
8	7.90	8.25	7.45	59.00	17.00	85.00	45.00	55.00
9	7.75	8.10	7.40	60.50	16.50	84.00	45.00	54.00
10	7.70	8.20	7.50	59.50	16.50	86.00	46.00	56.50
Average, Control	7.83	8.15	7.45	59.20	16.57	85.20	45.15	56.70
or real value.	7.90	8.22	7.42	61.5	16.25	72.00	40.00	34.00

I will not make any remarks on this table except that it has a comparative value of 95% altogether, or 97% in the first five series. With "spent liquors" and "barks" the results are equally satisfactory.

No.	Hemlock.	Oak.	Sumach.	Catechu.	Hemlock.	Oak.
1	.20	.250	1.50	1.95	1.50	.90
2	.20	.260	1.50	2.00	1.40	.95
3	.19	.250	1.50	2.00	1.50	.90
4	.21	.280	1.55	1.90	1.50	.90
5	.20	.250	1.50	1.95	1.40	.90
Average, Real value	.20	.255	1.51	1.96	1.46	.91
by control	.21	.270	1.62	1.90	1.50	.90

The first four are "spent liquors," the last two columns are of "spent bark."

Taking all these figures together and comparing the results with the working tests as under Lœwenthal's and Hammel's methods,

it will be found that they are within 5% of the real value in all the figures, and within 3% in the first five columns, oak, hemlock, etc. From this it may be seen that the error in the execution of this method in ascertaining the percentage of tannic acid in an oak, hemlock, sumach, etc., would not exceed one $\frac{1}{4}$ of one per cent., while in the estimation of catechu, kino, etc., the error is quite large. The cause of this is that the tannate of copper precipitated from these last materials is contaminated with considerable other matter, and besides this the peculiar principles present in these materials exert a solvent action upon the tannate of copper. This method may be used for these last determinations, but the kino may be more accurately determined by Löwenthal's method.

This method has been in use in my laboratory ever since I first investigated it, and the numerous analyses I am called upon to make of tanning materials and executed by it give the utmost satisfaction. I will continue to use it in all my leather researches now about to be commenced, also in commercial work. In conclusion I wish to tender my thanks to Mr. Jackson S. Schultz for valuable advice, and to all others who favored me with materials for this research, and facilitated it.

REVIEW OF INDUSTRIAL CHEMISTRY.

By A. A. BRENNEMAN.

SULPHURIC ACID.*—*Lunge* has undertaken to study against the phenomena of the lead chamber in order to test the conclusions put forward by R. Weber (†) in 1867 as to the action of SO_2 on NO and N_2O_5 . He finds that SO_2 and NO do not react upon one another, even at 100°C . when both are dry, but in presence of water they act slowly, the reaction requiring 48 hours for its completion at 15° . N_2O is formed, but the reduction does not extend further, no N being detected. Sulphuric acid of 1.45 sp-gr. does not hasten the reaction unless free O is also present. N_2O is produced in the latter case even when O is in excess of the amount required by the reaction $2 \text{SO}_2 + 2 \text{NO} + 3 \text{O} + 3 \text{H}_2\text{O} = 2 \text{H}_2\text{SO}_4 + 2 \text{HNO}_2$.

In the normal condition of the chamber both steam and O are in excess and a loss of nitrogen corresponding to the nitrate used in

(*) Ding. Jour. 243.1; Ber. D. Ch. Ges 14—2196. Chem. C. Bl. Dec. 7. '81.

(†) Ding. Jour. 184-246.