(8) The chemical composition of the different fractional coagula of the aqueous extracts of raw flesh is remarkably constant. They are also quite similar as regards their chemical constitution judging from the results of their hydrolysis.

(9) Raw flesh which has been completely freed from proteids soluble in cold water contains two classes of proteid substances, those which are soluble in a 10 per cent. solution of ammonium sulphate and those which are insoluble in this medium.

(10) Of the total proteids of lean raw flesh about 16.00 per cent. is insoluble in cold water but soluble in a 10 per cent. solution of ammonium sulphate.

(11) A 10 per cent. ammonium sulphate extract of flesh contains at least two individual proteids or groups of proteids which differ in physical properties and to some extent in chemical composition; one of them however may possibly be identical with the meat residue not dissolved by the ammonium sulphate.

(12) Raw flesh which has been completely freed from proteids soluble in cold water and also from those soluble in a 10 per cent. solution of ammonium sulphate is almost entirely soluble in a N/20 solution of potassium hydroxide.

(13) The proteid material of flesh insoluble in water and in a 10 per cent. solution of ammonium sulphate, but soluble in a N/20 solution of potassium hydroxide, has the same chemical composition even when separated from the solvent by different means and purified by widely differing treatment.

URBANA, ILLINOIS,
February 12, 1906.

[CONTRIBUTION FROM THE LEATHER AND PAPER LABORATORY OF THE BUREAU OF CHEMISTRY.][1]

THE EXTRACTION OF TANNING MATERIALS FOR ANALYSIS.[2]

BY F. P. VEITCH AND H. H. HURT.

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AT THE last meeting of the Association of Official Agricultural Chemists, a paper was presented on "The Extraction of Tanning Materials with Various Extractors," which was published in part in this Journal.[3] It was shown that in the hands of the

[1] By permission of the Secretary of Agriculture.

[2] Read at the New Orleans Meeting of the American Chemical Society.

[3] Veitch: This Journal, 27, 724.

TABLE I.—RESULTS WITH DIFFERENT EXTRACTORS.

No.	Sample.	Total extract. Koch. Per. cent.	Total extract. Continuous. Per cent.	Soluble solids. Koch. Per cent.	Soluble solids. Continuous. Per cent.	Reds. Koch. Per cent.	Reds. Continuous Per cent.	Non-tannins. Koch. Per cent.	Non-tannins. Continuous. Per cent.	Tannins. Koch. Per cent.	Tannins. Continuous. Per cent
"R"	Sumac, Sicily.....	....	51.22	44.53	47.94	....	....	20.02	20.93	24.51	27.01
75	Sumac, Sicily.....	40.64	48.88	38.39	45.13	2.25	3.65	17.88	21.02	20.25	24.11
76	Sumac, Sicily.....	41.58	54.42	39.80	48.86	1.78	5.56	22.30	24.01	17.50	24.85
80	Sumac, Sicily.....	50.14	58.37	48.16	56.34	1.98	1.93	21.82	27.10	26.34	29.24
437	Sumac, Sicily.....	53.87	60.13	49.35	59.97	4.52	0.16	17.65	24.05	31.70	35.92
132	Lentiscus, Sicily.....	37.65	45.06	34.89	39.13	2.76	5.93	19.23	22.73	15.66	16.40
69	Leaves A. manzanita, Calif.	40.65	50.24	39.75	48.17	0.90	2.07	25.41	32.21	14.34	15.96
314	Chestnut oak bark	18.30	20.84	16.86	19.27	1.44	1.57	6.85	7.58	10.01	11.69
316	Canaigre	52.91	55.30	46.73	48.75	6.18	6.55	15.20	15.96	31.73	32.79
315	Quebracho wood	26.13	28.55	24.40	27.14	1.73	1.41	2.38	2.72	22.02	24.34
385	Quebracho wood	28.93	32.68	24.84	27.90	4.09	4.78	....	3.41	....	24.49
	Quebracho wood	32.32[1]	31.63	28.12	27.43	4.20	4.20	3.96	2.98	24.16	24.45
386	Spent hemlock bark	9.30	10.94	8.41	9.04	0.89	1.90	4.28	3.98	4.13	5.06
438	New hemlock bark	16.47	23.35	15.53	20.99	0.84	2.36	4.64	7.31	10.89	13.58
781		63.12[2]	71.43	59.59	64.00	3.53	7.43	18.74	21.12	40.85	42.88
		65.54	71.78	60.96	64.76	4.58	7.02	21.68	20.78	39.28	43.98
	Chestnut wood.....	13.68[1]	12.50	12.28	11.20	1.40	1.30	4.75	3.63	7.43	7.57
		8.98	15.30[3]	8.53	13.83	0.40	4.47	2.25	4.88	5.28	8.95

[1] Weiss extractor. [2] Results by Krug. [3] Ground to 1 mm.

writer a continuous extractor such as the well known double tube, or that devised by Zulkowsky, gave more complete extraction and higher tannins than the Weiss or the Koch extractor, which are almost universally used in extracting tanning materials. In addition, this continuous extractor possesses the advantages of avoiding long boiling of the extract, undue concentration of the extract, and a saving in time required to concentrate dilute liquor. It has the further advantage of being more rapidly manipulated and is longer lived than some forms, while it is cheaper than other extractors that are used or have been proposed.

The results here reported are a continuation of the work then started, undertaken to determine if the continuous extractor gave different results from other extractors. For convenience, some of the results reported in the previous paper are included here, that the data on the commonly used material may be all together. All materials in the table were ground to pass through a 2 mm. mesh sieve.

It will be seen that without exception the results with the continuous extractor are higher than with any of the old forms in which the extraction was continued for a longer time than is customary. It was found necessary to continue the extractions with the Weiss extractor for from two to four days and the volume of extract was from 3 to 6 liters. It is possible of course that the long boiling, necessary to concentrate the last portions of these extracts, destroyed some tannin, a contingency which would have lowered the tannin figures by the Weiss method. But even under this long extraction all tannin was not removed from the materials, for upon transferring the residues to the continuous extractors a heavy precipitate of tannin was obtained in the extract, thus showing that tannin still remained in the material and indicating at the same time that the destruction of tannin by boiling had been small if any.

The results by the two methods on sumac and on canaigre are worthy of more than passing mention, as it has been held by many investigators that in extracting these materials the temperature must be kept at from 50° to 60° C. until at least half the volume of the extract is obtained, when it is permissible to raise the temperature. With the continuous extractor it is our

custom to extract with from 200 to 300 cc. of water below 100° C. and finish the extraction at steam heat. It seems to the writers that the reasons advanced for the extraction of certain materials at low temperature are not good ones. If all the tannin is not removed in the extract obtained at low temperature, there is every reason to believe that the gelatinization of the starch at high temperatures would prevent the extraction of the remaining tannin or possibly precipitate a portion of the extracted tannin. That this is not so, is evidenced by the results with the continuous extractor and also by the fact that even with the old form of extractor much tannin is removed on increasing the heat. However, speculation on these points is of little value as it is probable that complete extraction of any material by the older methods, except by the use of the Soxhlet, has seldom been obtained and was certainly not obtained in these experiments. We are convinced, however, that a Soxhlet which does not require too great concentration of the extracted material between the siphonings will give complete extraction and higher tannin; but with so large a charge as is generally used in this work the Soxhlet is likely to become continuous in operation. Undue concentration of the liquors is best prevented by the removal of the liquors and their replacement by water after the extraction has proceeded but a short time.

No indication as to the condensation of tannins to reds can be obtained from the figures given, as in nearly all cases where the continuous extractor was used some finely ground material passed into the extract. In some cases, however, the reds are as low as with the Koch extractor, indicating no greater change in these cases than with the Koch extractor. This is true with sumac, with chestnut oak bark, with quebracho wood and with canaigre, the last three of which, being representative of catechol tannins, would be most likely to show such change.

As a further test of various methods of extracting, samples of sumac and of oak bark which were ground to pass a 2 mm. mesh were extracted in several ways.

(1) By the Proctor extractor, beginning the extraction at 50° and gradually raising the temperature to 100°, the extraction being discontinued when 1 liter was reached, at seven hours.

(2) By the continuous extractor for the same time.

(3) By the continuous extractor for sixteen hours.

(4) By the Soxhlet extractor for sixteen hours, removing the extracted material as in the continuous method.

The results are given in Table II.

TABLE II.—EXTRACTION OF SUMAC AND OAK BARK BY DIFFERENT METHODS.

Material.	Method of extraction.	Total extract.	Soluble solids.	Reds.	Non-tannin.	Tannin.
Sumac No. 420	Continuous, 16 hours	57.00	53.85	3.15	19.80[1]	34.05
Sumac No. 420	Continuous, 7 hours	53.45	51.27	2.18	17.97[1]	33.30
Sumac No. 420	Siphon Soxhlet, 16 hours .	54.69	51.63	2.06	17.53[1]	34.10
Sumac No. 420	Proctor, 7 hours to 1 liter.	48.33	46.78	1.54	16.60[1]	30.19
Oak bark No. 314	Continuous, 16 hours	21.69	19.76	1.93	7.96[2]	11.80
Oak bark No. 314	Continuous, 7 hours	19.23	17.63	1.60	6.65[1]	10.98
Oak bark No. 314	Siphon Soxhlet, 16 hours .	19.57	18.29	1.28	7.09[1]	11.20
Oak bark No. 314	Proctor, 7 hours to 1 liter.	15.25	14.91	0.34	5.77[1]	9.14

With these materials the continuous extractor for sixteen hours and the siphon extractor (which in reality acted as a continuous extractor) gave practically the same results on tannin. The continuous extractor that was run for the same length of time that was required to collect 1 liter with the Proctor extractor gave slightly lower results, while the Proctor extractor, extracting but 1 liter, gave the lowest results, and in both cases the extract then coming through was colored and gave a heavy precipitate with gelatine solution. It is quite evident that by the latter method extraction was far from complete and that decidedly better results are obtained with the continuous extractor run for the same length of time.

The sample marked "R" furnishes much evidence on the difficulty of completely extracting tanning materials by the accepted procedure. This sample was submitted to the senior author in 1901 for analysis and gave the figures given under the "Koch" heading in Table I. The results by the continuous extractor were secured recently by Mr. Hurt. At the time the sample was submitted in 1901 it was also analyzed by another chemist, using the Proctor or Weiss form of extractor, who reported total extract 39.86 per cent., soluble solids 35.98 per cent., non-tannins 18.34 per cent. and tannin 17.64 per cent., showing that the extraction was far from complete. To secure more light on extraction, another sample of sumac was treated as follows, using the Koch extractor for the work. In all experi-

[1] No tannin in filtrate.

[2] Tannin in filtrate.

ments, the first 500 cc. of percolate were secured in from one and one-quarter to two hours at from 60° to 70° C. The balance secured at steam heat was concentrated to the desired volume.

Experiment I.—Twenty grams extracted, total percolate $3\frac{1}{2}$ liters. After last half liter, percolate still gave slight opacity with gelatine solution.

	Per cent.
Total extract	48.72
Soluble solids	47.50
Non-tannins	20.38
Available tannin	27.12

Experiment II.—Twenty grams extracted, percolate 4 liters, concentrated to 1 liter. No apparent opacity with gelatine after the last $\frac{1}{2}$ liter of percolate, but still gave a distinct color with ferric sulphate.

	Per cent.
Total extract	51.95
Soluble solids	47.10
Non-tannins	17.90
Available tannin	29.20

Experiment III.—Twenty grams extracted with 2 liters of water, the last 1500 cc. being boiled down to 500 cc. and added to the first 500 cc. Time of extraction about seven hours.

	Per cent.
Total extract	45.67
Soluble solids	43.10
Non-tannins	16.76
Available tannin	26.34

Percolate after the last $\frac{1}{2}$ liter showed tannin with gelatine.

Experiment IV.—Continued the extraction of the 20 grams used in Expt. III, percolated 2 liters at temperature of boiling water, after which the test with gelatine was uncertain, but color was strong with ferric sulphate. Boiled down the 2 liters to $\frac{1}{2}$ liter and made analysis. Time of extraction about three hours.

	Per cent.
Total extract	5.00
Soluble solids	3.58
Non-tannins	1.76
Available tannin	1.82

Experiment V.—The percolation of the same 20 grams sample used in Expts. III and IV was continued until 4 liters more water had been percolated, when the percolate was boiled down to $\frac{1}{2}$

liter and analyzed as in Expts. III and IV. Time of extraction about six hours.

	Per cent.
Total solids	3.37
Soluble solids	2.39
Non-tannins	1.03
Available tannin	1.36

Adding results of Expts. III, IV and V we have a total of

	Per cent.
Total extract	54.04
Soluble solids	49.07
Non-tannins	19.55
Available tannin	29.52

extracted by 8 liters of water at about 100° C. in about sixteen hours. The residues from these extractions were dried and amounted to 37.20 per cent.

	Per cent.
Residue	37.20
Moisture in sample	7.93
Total extract	54.04
	99.17
Amount of sample lost in analysis	0.83.

These results show that extraction of tannin was not complete with percolation of 3½ liters of water, but was practically complete with 4 liters and that 8 liters removed but little more tannin but did remove more soluble non-tannins.

EFFECT OF FINENESS OF MATERIAL.

The size of the particles of the material to be extracted will certainly influence the time required for complete extraction. Some data on this point are shown in Table III.

Time of extraction about eighteen hours.

TABLE III.—RESULTS ON MATERIALS OF VARYING FINENESS.

Fineness of sample.	Total extract. Per cent.	Soluble solids. Per cent.	Non-tannins. Per cent.	Tannin. Per cent.
Quebracho wood ground to 4 mm. mesh	29.30	26.24	3.17	23.07
Quebracho wood ground to 2 mm. mesh	32.68	27.90	3.41	24.49
Quebracho wood ground to 1 mm. mesh	31.14	27.43	3.31	24.12
Spent hemlock bark ground to 2 mm. mesh	11.10	....	4.20	....
Spent hemlock bark ground to 1 mm. mesh	10.94	9.04	3.98	5.06
Chestnut wood ground to 4 mm. mesh	15.30	13.83	4.88	8.95
Chestnut wood ground to 1 mm. mesh	16.07	13.81	4.96	8.84

In all cases a trace of tannin could be detected on further extracting the materials.

The results given in this paper confirm the conclusions previously drawn that the continuous extractor has given the most complete extraction and that by this apparatus all soluble constituents are removed in larger quantities than by other extractors. It may be said, however, that while we believe this to be the best extractor with which we are acquainted, it is not to be doubted that other forms can be made to give as complete extraction, but at a greater expenditure of money, time, and labor.

We desire especially to call attention to the necessity for complete extraction. With the comparatively large quantity of material that is used it is exceedingly difficult to secure this. All materials should be ground to pass at most a millimeter sieve, and extraction should be continued for at least sixteen hours, preferably for twenty-four hours. The efforts of this laboratory are now being directed toward so modifying the methods of tannin analysis that smaller quantities of material may be used and thus secure more complete extraction.

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THE EXAMINATION OF WRITING INKS.[1]

BY L. S. MUNSON.

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IN many branches of the government service as well as in many state and private institutions it is frequently of particular importance that permanent records be preserved, and from necessity or convenience many of these are written records. It is well known that many of the old writing fluids yielded records that have remained unchanged for generations, and undoubtedly many of the writing inks in use at the present time are equally resistant. However, from the great advances made in recent years in the manufacture of colors has arisen the tendency to substitute these colors in whole or in part in the manufacture of ink. This investigation was taken up, therefore, to determine to what extent the inks in use in the different executive departments were suitable for record purposes.

[1] Read at the New Orleans Meeting of the American Chemical Society.