

	I. Gram.	II. Gram.	III. Gram.	IV. Gram.	V. Gram.	VI. Gram.	Taken. Gram.
Total weight of cou- marin (by difference)	0.0752	0.0715	0.0713	0.0707	0.0732	0.0723	0.0750
Weight of residue con- taining vanillin and acetanilide	0.0928	0.0917	0.0906	0.0908	0.0900	0.0922	
Weight of acetanilide. .	0.0216	0.0192	0.0145	0.0168	0.0156	0.0161	
Total weight of vanillin (by difference)	0.0712	0.0725	0.0761	0.0740	0.0744	0.0761	0.0750
Total weight of acet- anilide	0.0769	0.0727	0.0704	0.0723	0.0707	0.0716	0.0750

The purity of the coumarin, vanillin and acetanilide as weighed out, also as recovered in the course of the analyses, was established by determination of melting-points.

The amounts of the three substances used were in each case 0.0750 gram, equivalent to about 0.3 per cent. of the extract. The error in the determination of each in no case reached 0.0050 gram, equivalent to about 0.02 per cent.

[CONTRIBUTION FROM THE LEATHER AND PAPER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.
SENT BY H. W. WILEY.]

THE EXTRACTION OF TANNING MATERIALS WITH VARIOUS EXTRACTORS.¹

BY F. P. VEITCH.

Received March 18, 1905.

OWING to the fear that tannin may be oxidized by prolonged boiling, and to the fact that the extraction of certain materials gives maximum results only at low temperatures, a number of forms of apparatus have been used for the laboratory extraction of tanning materials. At present, however, but two extractors are in general use: the Koch or some modification of it, as that of Proctor, and a modified Soxhlet, devised at the Vienna Research Laboratory, and generally known as the Weiss extractor.

There are several objections to each of these extractors. With the Koch extractor, the evaporation of the extract, which amounts to 2 to 4 liters, is a decidedly objectionable feature, requiring considerable time, and encouraging to a certain extent, the very thing it was designed to prevent, namely, the oxidation of the

¹ Read before the Association of Official Agricultural Chemists, St. Louis, October 1904.

tannins by boiling. In addition, there is reason to believe that where the tanning material is put in the extractor dry, the most convenient way, there is often some channelling, and the extraction is incomplete, as illustrated in the case of the spent hemlock bark given in the table. On the other hand, the Koch apparatus enables one to control the temperature of extraction as no other form now in use does, and for this reason, especially, has its use seemed to be advisable with materials high in starch. Notwithstanding the fact that Eitner *et al.*,¹ found that the Weiss extractor gave satisfactory results, tanning chemists have generally looked with misgiving on it, fearing oxidation during the long-continued boiling of the strong extract. Indeed, Palmer,² Procter and Parker,³ and Parker⁴ have found that from many materials less tannin is extracted at boiling than at a lower temperature. The total volume of extract in these experiments was only 1 liter, however, and it seems possible that longer extraction would have given more tannin at the higher temperatures.

The International Association of Leather Trades Chemists has adopted the Koch (or Procter) extractor as official, and Procter⁵ regards the prolonged boiling of the extracted materials, such as takes place in the Weiss extractor, as inadmissible.

On the other hand, in addition to Eitner *et al.*, Bough⁶ has found that the Weiss extractor gave higher results than the Koch extractor on oak, and pine bark, valonia, sumac, and Quebracho wood, and gave lower results on divi-divi and Myrobalans. The Weiss extractor is used in most tannery laboratories in this country in extracting woods and barks.

It will thus seem that there is considerable difference of opinion as to the accuracy of the results and the losses of tannin obtained with these two methods of extraction. I have, therefore, endeavored to avoid the difficulties and objections presented by these generally used methods, by substituting an extractor with which the evaporation and concentration of large volumes of dilute liquors, obtained by the Koch method, is avoided, and with which the prolonged boiling of the gradually strengthening extract and its frequent concentration and dilution, as with the

¹ Der Gerber, 1887, p. 3.

² See Procter's "Principles of Leather Manufacture," p. 344.

³ *Jour. Soc. Chem. Ind.*, 14, 635.

⁴ *Ibid.*, 17, 106 (1898).

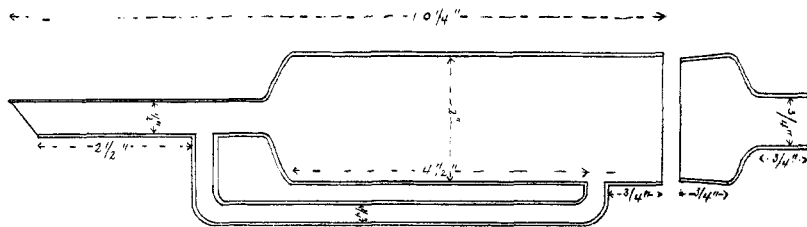
⁵ Vide "Leather Industries Laboratory Book, and Principles of Leather Manufacture."

⁶ *Abstract J. Soc. Chem. Ind.*, 18, 303 (1899).

Weiss, is not necessary. Such an extractor is found in the old and well-known double tube continuous extractor, or in the side tube extractor devised by Zulkowsky. With the former, the extraction takes place at 95° - 100° C., with the latter at 90° - 95° . Undue concentration and boiling of the extract is avoided by placing only about 250 cc. of water in the receiving flask, and after the extraction has continued a short time, replacing the receiving flask by another containing the same amount of water. This is repeated at longer intervals, until the extraction is completed, the total volume of extract being kept within a liter.

When it is desired to extract the first portions at temperatures below boiling, it is only necessary to allow water of the given temperature to flow slowly into the filled extractor, and to continue the percolation until 500 cc. of extract have been obtained. Water is then placed in the receiving flask, and the extraction finished at steam heat.

The extractor is sufficiently described in the accompanying drawing. The extractor may be made of glass or tinned copper. When glass is used, it should be of such a character as not to yield appreciable quantities of alkalis to steam on prolonged boiling, as the soluble solids are affected thereby. It is difficult to get a side tube extractor of glass that will stand a temperature of 100° C., so that copper extractors are most satisfactory.



In loading the extraction tube a perforated porcelain disk is first placed in it, and the weighed material, previously mixed with water to a thin paste, is washed into the extractor, and gently pressed down in order to make it fairly firm. Another perforated porcelain disk is placed on top of the material. The cloudy extract, which has passed through into the receiving flask, is returned to the extractor, which is then connected with the condenser. The perforated disk on top of the material distributes the con-

densed water, and is prevented from rising above the entrance of the side tube by coming in contact with the end of the condenser tube, which should come down to this point. This prevents escape and loss of material, which is apt to be caused by the expansion of the air and steam in finely ground materials. Wetting the material before putting it in the extractor prevents channelling, and insures regular extraction.

Comparative results, which have been obtained with all three forms of extractor, are given in the table. The time of extraction was the same with all extractors, and it was found necessary to continue it for two working days, or about fifteen hours with the Koch extractor, when extraction was discontinued with all.

The results marked (1) were obtained with the Weiss, (2) with the Koch, and (3) with the continuous extractor. The samples include the most generally used native tanning materials, except chestnut and oak bark.

RESULTS OBTAINED WITH DIFFERENT EXTRACTORS.

Material.	Ex-tractor.	Total extract. Percent.	Soluble solids. Percent.	Reds. Percent.	Non-tannin. Percent.	Tannin. Percent.
Bark of Tan bark oak.....	1	27.04	26.06	0.98		
	2	27.38	26.82	0.56	10.60	16.22
	3	29.66	28.68	0.98		
Bark of Tan bark oak "rump bark"	1	45.76	43.72	2.04		
	2	44.92	42.06	1.86	12.86	19.20
	3	47.64	45.48	2.16		
Pecan shells.....	1	12.72	12.08	0.64		
	2	11.36	1.73	9.63
	3	13.24	12.52	0.72		
Hemlock bark new	1	18.47	16.10	2.17		
	2	17.43	15.63	1.80	4.75	10.88
	3	23.10	19.37	3.73	7.48	11.89
Hemlock bark, spent	1
	2	3.06	2.93	0.13	1.57	1.36
	3	8.29	7.24	1.05		
Chestnut wood.....	1	13.68	12.28	1.40	4.75	7.43
	2	8.98	8.53	0.40	2.25	5.28
	3	12.50	11.20	1.30	3.63	7.57
Sumac leaves, course ground.	1	52.05	49.70	2.35	28.54	21.16
	2	47.42	45.72	1.70	20.74	24.98
	3	53.57	49.85	3.72	27.29	22.56
" " fine ground...	3	53.12	49.70	3.42	25.92	23.78

In examining the results, total extract may be omitted from consideration, as this determination often includes some of the material, which was mechanically carried over into the extract. This is particularly true with the results from the Weiss extractor. Although the solid material was given time to settle before drawing out for total solids, not much importance is attached to figures for total extract.

The figures show how radically the results may differ under different conditions of extraction.

Soluble solids were highest by the continuous extractor, except in the case of chestnut wood, where I believe the coarseness of the sample was in favor of the Weiss extractor. The Weiss extractor gives higher results than the Koch extractor, except on one sample of Tan Oak bark. Tannin is highest with the continuous extractor, except with sumac, where, notwithstanding the lowest soluble solids, tannin is the highest, when the Koch extractor was used.

As a rule, it appears that where the extraction is continued for some time, all constituents, reds, non-tannin, and tannin, are removed in somewhat larger quantities by using a continuous extractor. Except in the case of sumac, there is nothing to indicate that there is any serious loss of tannin, or, perhaps we should say, any material difference in the loss of tannin from any cause, with any of the extractors. While reds and non-tannin are usually higher when the continuous extractor is used, this fact, in the face of high tannin, is not conclusive evidence, that any loss of tannin has occurred. As has been said, apparently larger amounts of all soluble constituents have been dissolved.

The conflicting results obtained from the different investigations on the effect of heat on the extraction of tannin and on its oxidation, renders further investigation very desirable. I am convinced, that the chief explanation of these conflicting results is to be found in imperfect extraction, due to the small quantity of water usually passed through the Koch apparatus, and to too few siphonings with the Weiss. Procter and Parker in their investigation of the effect of temperature used only one liter of water, and text-books generally give one to understand that complete extraction may be secured with two liters or less of water. My experience leads me to doubt this very much, as I usually find

tannin being removed in considerable quantities, after extracting with three or four liters during eight to twelve hours.

This investigation will be continued, and extended to include other tanning materials.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

DETERMINATION OF SULPHUR AND PHOSPHORIC ACID IN FOODS, FECES AND URINE.

BY W. L. DUBOIS.

Received March 20, 1905.

IN a previous contribution¹ from the Bureau of Chemistry, the methods then in use for the determination of sulphur and phosphoric acid in connection with the metabolism experiments being conducted by Dr. Wiley and Dr. Bigelow were described. Since the appearance of that article, some important changes in the method of burning foods and feces have been made, to which I wish to call attention. Urines are still burned by Osborne's method, the facility of handling them in that way being all that could be desired. In this work all phosphoric acid determinations were made by Mr. C. W. Nelson.

For foods and feces we are now using a modification of a method recently described by Neumann and Meinertz.² In adapting this method to foods and feces we doubled the initial amount of sodium peroxide, owing to the larger sample used. It was found that moist foods, *e. g.*, meats and eggs, burned without difficulty, whereas dried foods and feces gave a good deal of trouble by frequent flashing. Since the most marked difference in these two classes of material is in their water content, we found that the addition of a small amount of water to the dried charges caused the combustion to proceed smoothly. Experience showed that the use of sodium carbonate alone, instead of a mixture of sodium and potassium carbonate, is more satisfactory, because the fusion with the former is more rapidly dissolved from the crucible by hot water, although as far as accuracy of results is concerned, we noticed no difference whether using sodium carbonate, potassium carbonate,

¹ This Journal, 26, 1108.

² *Z. physiol. Chem.*, 43, 37.