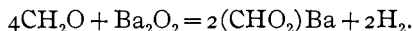


very slow and incomplete. When heated, a quantitative reaction seems to take place:



The reaction takes place more readily in the presence of free hydrogen peroxide. The results, however, were lower than with sodium peroxide. An average of five analyses with sodium peroxide gave 34.88 per cent. of formaldehyde, while with barium peroxide and hydrogen peroxide an average of 32.9 per cent. was obtained.

THE ACTION OF MANGANESE AND LEAD PEROXIDES ON FORMALDEHYDE.

The dioxides of manganese and lead are practically inert with formaldehyde alone. If hydrogen peroxide is added, as in the case of barium peroxide, oxygen, instead of hydrogen, is liberated. The amount of oxygen seems to be entirely independent of the presence of formaldehyde. The reaction seems however to be more vigorous in the presence of formaldehyde. Further examination is being made.

That the reaction which takes place between formaldehyde and hydrogen peroxide in alkaline solution is quantitative, there can be no doubt. Several things must be taken into consideration, however, in order that accurate results may be obtained. Special attention must be given to temperature, as considerable heat is generated in the reaction. The quantities of the reagents also vary the results. Large amounts of hydrogen peroxide and potassium hydroxide give higher results than moderate amounts of the reagents. This may be remedied, however, by diluting the reagents.

With proper care in manipulation very concordant results may be obtained, and the presence of formic acid, methyl alcohol and other impurities do not interfere or change results.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE DETERMINATION OF VANILLIN, COUMARIN AND ACETANILIDE IN VANILLA EXTRACT.

BY A. L. WINTON AND E. MONROE BAILEY.

THE Hess and Prescott method¹ for the determination of vanillin and coumarin soon after its appearance, was adopted as a

¹ This Journal, 21, 256 (1899).

provisional method by the Association of Official Agricultural Chemists, and has come into general use in American food laboratories. Winton and Silverman¹, working with extracts made in the laboratory from pure vanillin and coumarin, found that this method, slightly modified, gave remarkably accurate results for vanillin, and reasonably accurate results for coumarin. When, however, as high as 0.30 per cent. of coumarin was present, there was a deficiency of 5 to 10 mg., equivalent to 0.02 to 0.04 per cent. of the extract.

This slight loss of coumarin, we have since found, was sustained during de-alcoholizing, and may be largely or entirely obviated by following the instructions given on page 722, thus avoiding over-concentration. The loss of coumarin from a concentrated solution is so great as to render the analysis entirely worthless. For example, in evaporating 25 cc. of an extract containing 0.30 per cent. of coumarin three times to a volume of 10 cc., this loss amounted to over half the total quantity present.

Adulteration of Vanillin with Acetanilide.—In a circular, issued by a well-known chemical house in 1901, attention was called to low-priced vanillin then on the market, sold usually under foreign labels, which, according to analysis, was adulterated with 35 per cent. of acetanilide. It was further stated that this practice was not only dishonest, but a menace to health, and that the house would analyze free of charge suspected samples.

None of the commercial vanilla extracts analyzed at this Station, during the year 1901, contained acetanilide, although many of them were unquestionably made from synthetic vanillin, but during the present year 4 out of 47 adulterated extracts examined, contained amounts ranging from 0.08 to 0.15 per cent. The percentages of vanillin, coumarin and acetanilide in these samples, and the melting-points of the acetanilide, were as follows:

DETERMINATIONS OF VANILLIN, COUMARIN AND ACETANILIDE IN COMMERCIAL VANILLA EXTRACTS.

Serial number.	Vanillin. Per cent.	Coumarin. Per cent.	Acetanilide. Per cent.	Melting-point of acetanilide. Degrees C.
12806	0.35	0.06	0.13	113
12903	0.21	0.04	0.08	113
12907	0.31	0.00	0.13	112
12911	0.19	0.00	0.15	112

¹ This Journal, 24, 1128 (1902).

These results indicate that these extracts were made from vanillin containing from 27 to 45 per cent. of acetanilide.

Detection of Acetanilide.—This adulterant is readily detected in the course of Hess and Prescott's process by the incomplete solubility in petroleum ether of the residue, which in the case of extracts free from acetanilide is pure coumarin, by the melting-point of the insoluble portion (112° C.), and by its qualitative reactions. The weighed residue of coumarin and acetanilide is stirred for fifteen minutes with 15 cc. of petroleum ether, the clear solution is carefully decanted, and the operation of stirring and decanting is repeated three times. This we have found sufficient in all cases for complete solution of the coumarin without dissolving appreciably the acetanilide.

The residual acetanilide is dried in a desiccator, weighed, and tested as to its melting-point and reactions. The weight deducted from the weight before dissolving out the coumarin, gives the weight of the coumarin. The extract is allowed to evaporate at room temperature, and the melting-point of the crystals determined. If desired, the coumarin can be weighed, but it is more accurate and convenient to obtain this ingredient by difference.

We have found the following qualitative reactions recommended by Ritsert,¹ to be reliable:

Boil the residue in a small beaker for two or three minutes with 2 to 3 cc. of concentrated hydrochloric acid, cool, divide into three portions, and test in small tubes (4 to 5 mm. inside diameter) as follows:

(1) Indophenol reaction. To one portion add carefully 1 to 3 drops of a solution of chlorinated lime (1 : 200) in such a manner that the two solutions do not mix. A beautiful blue color formed at the juncture of the two liquids indicates acetanilide.

(2) To another portion add a small drop of permanganate solution. A clear, green color is formed, if any appreciable amount of acetanilide is present.

(3) Mix the third portion with a small drop of 3 per cent. chromic acid solution. Acetanilide gives a yellow-green solution, changing to dark green on standing five minutes, and with the formation of a dark blue precipitate on addition of a drop of caustic potash solution.

We have not found the indophenol test adopted by the German

¹ *Pharm. Ztg.*, 33, 383; *Abs. Z. anal. Chem.*, 27, 667 (1888).

Association of Pharmacists¹ so satisfactory as Ritsert's modification, as blank tests often give a blue color, due probably to impurities in the phenol employed.

Method of Determining Vanillin, Coumarin and Acetanilide.—The following modification of the Hess and Prescott method gives satisfactory results for all three substances:

Weigh out 25 grams into a 200 cc. beaker with marks showing volumes of 25 and 50 cc. Dilute to the 50 cc. mark, and evaporate in a water-bath to 25 cc. at a temperature in the bath of not more than 70° C. Dilute a second time to 50 cc., and evaporate to 25 cc. Add normal lead acetate solution drop by drop until no more precipitate forms. Stir with a glass rod to facilitate flocculation of the precipitate, filter through a moistened filter, and wash three times with hot water, taking care that the total filtrate does not measure more than 50 cc. Cool the filtrate, and shake with 20 cc. of ether in a separatory funnel. Remove the ether to another separatory funnel, and repeat the shaking of the aqueous liquid with ether three times, using 15 cc. each time. Shake the combined ether solutions four or five times with 2 per cent. ammonia, using 10 cc. for the first shaking, and 5 cc. for each subsequent shaking. Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish, and allow the ether to evaporate at the room temperature. Dry in a desiccator, and weigh. Stir the residue for fifteen minutes with 15 cc. of petroleum ether (boiling-point 30° to 40° C.), and decant off the clear liquid into a beaker. Repeat the extraction with petroleum ether two or three times. Allow the residue to stand in the air until apparently dry, completing the drying in a desiccator. Weigh, and deduct the weight from the weight of the residue obtained after the ether evaporation, thus obtaining the weight of the coumarin. This residue, if acetanilide, should have a melting-point of about 112° C., and respond to the qualitative tests already given.

Allow the petroleum ether extract to evaporate at room temperature. If it is pure coumarin, it should have a melting-point within a few degrees of 67° C., and respond to Leach's test.²

Slightly acidulate the ammoniacal solution, reserved for vanillin, with 10 per cent. hydrochloric acid. Cool, and shake out in

¹ *Z. anal. Chem.*, **27**, 666 (1888).

² "Food Inspection and Analysis," p. 732.

a separatory funnel with four portions of ether, as described for the first ether extraction. Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh.

If acetanilide has not been previously detected, this residue should be pure vanillin, with a melting-point within a few degrees of 80° C.

If acetanilide has been detected, dissolve the residue in 15 cc. of 10 per cent. ammonia, and shake out twice with an equal volume of ether. Evaporate the ether solution at room temperature, dry in a desiccator, and weigh. Deduct this weight from the previous weight, thus obtaining the weight of pure vanillin. The total weight of the acetanilide is obtained by adding the weight of this last extract to that of the residue previously obtained, and identified as acetanilide.

In doubtful cases the ammoniacal solution should be acidified, shaken out with ether, and the melting-point of the vanillin, obtained by evaporation at room temperature, determined.

It is quite possible that the first shaking with ammonia would effect a complete separation of vanillin from both coumarin and acetanilide, if a smaller amount of ammonia of greater strength were used, as first proposed by Hess and Prescott. We have found, however, that the more dilute ammonia is much more satisfactory for ordinary extracts free from acetanilide, and it seems, therefore, undesirable to modify the process to fit exceptional samples.

Test Analyses.—In order to test the accuracy of the above-described process, an extract was prepared in the laboratory containing 20 per cent. of cane-sugar, 40 per cent. of alcohol, and in each 25 cc., 0.0750 gram each of pure vanillin, coumarin and acetanilide. The results obtained on six 25-cc. portions of this extract are given in the following table:

ANALYSES OF AN ARTIFICIAL VANILLA EXTRACT CONTAINING KNOWN AMOUNTS OF VANILLIN, COUMARIN AND ACETANILIDE.

	I.	II.	III.	IV.	V.	VI.	Taken.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
Weight of residue containing coumarin and acetanilide	0.1305	0.1250	0.1272	0.1262	0.1283	0.1278	
Weight of acetanilide	0.0553	0.0535	0.0559	0.0555	0.0551	0.0555	

	I.	II.	III.	IV.	V.	VI.	Taken.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
Total weight of coumarin (by difference)	0.0752	0.0715	0.0713	0.0707	0.0732	0.0723	0.0750
Weight of residue containing 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 acetanilide	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.

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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.