and their anilides. The titration of 2,4-dichloroaniline with 0.1 *N* sodium nitrite in the presence of hydrochloric acid at 25° C. was found to proceed rapidly, giving a purity of 99.6 per cent for material prepared as described above. The presence of the 2,4-dichloroacetanilide had no effect upon the titration of the 2,4-dichloroaniline.

Procedure

(*a*) Weigh into a 300-cc. Erlenmeyer flask 2.000 grams of 2,4-dichloroaniline and add 25 cc. of glacial acetic acid. Weigh carefully from 0.6 to 0.7 gram of acetic anhydride (100 per cent) in a small glass-stoppered weighing bottle. Remove the stopper from the bottle and lower the bottle into the Erlenmeyer, stopper the flask, and rotate it so as to wash the anhydride out of the bottle. Allow the flask to stand at 25° C. for 1 hour.

Transfer the solution to a 400-cc. beaker, using 150 cc. of water containing 25 cc. of 35 per cent hydrochloric acid at 15° to 20° C. Adjust the temperature of the solution to 20°–25° C. and titrate the excess dichloroaniline with 0.1 *N* sodium nitrite, using a 1-minute end point with potassium iodide starch papers (*M*). The dichloroacetanilide present does not interfere, provided the temperature is kept below 26° C. and the titration is completed within 1 hour of the time of dilution of the acetylation mass.

(*b*) Weigh carefully 0.9 to 1.0 gram of the dichloroaniline, and proceed as above with the exception that no anhydride is added. Titrate with 0.1 *N* sodium nitrite as above (*L*).

(*c*) Determine the amount (*O*) of 0.1 *N* sodium nitrite required to give a test for nitrous acid in the same volume of water, hydrochloric and acetic acids used in the above determinations.

Calculations

$$\frac{(L-O) \times \text{wt. of dichloroaniline used in } (a)}{\text{Wt. of dichloroaniline used in } (b)} = \text{Cc. of NaNO}_2$$

equivalent to the total dichloroaniline used in $(a) = P$

$$\frac{P - (M - O) \times N \times 10.21}{\text{Wt. of sample of acetic anhydride}} = \text{Per cent of acetic anhydride}$$

Results

Proceeding according to this method, samples of pure and of commercial acetic anhydride were analyzed, with the results shown in the Tables IV and V. The acetic acid was determined by the method of Walton and Withrow.[2]

Acetone by Distillation of Wood with Lime[1]

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The utilization of wood waste is still largely an unsolved problem. The wood distillation industry, hitherto one of the largest consumers of small-dimension refuse, is threatened in its very existence by the synthesis of acetic acid from acetylene, methanol from carbon monoxide and hydrogen, and the production of acetone in the butyl fermentation of starch.

Within recent years considerable work has been done on the distillation of wood in the presence of various chemicals in order to increase the yield of valuable products. The most striking statement is that of Basset,[2] who claimed a yield of 26 per cent of acetone and mixed ketones by distilling wood with 2.5 parts of lime. Hawley,[3] using up to 60 per cent of lime, did not obtain an increase in acetone, the yield varying from 0.01 to 0.05 per cent. Fremy[4] in 1835 showed that acetone was obtained by distilling sugar, gum, and starch with 8 parts of lime. No yields of acetone were given and, contrary to the statement of Basset, Fremy does not mention having used wood.

Several experiments were made to determine the yield of acetone from wood and modified celluloses. From 25 to 75 grams of material passing a 40-mesh sieve were thoroughly mixed with 4 parts of hydrated lime and distilled from an iron retort having a capacity of 1.3 liters. Preliminary trials with starch showed no increase in acetone by increasing the lime to 8 parts. The retort was gradually brought to a temperature of 500° C. over a distillation period of 7 to 8 hours.

The distillate obtained was redistilled three times, twice after having been made slightly alkaline with sodium hydroxide, and finally in the presence of a small amount of sulfuric acid. About 70 per cent of distillate was collected each time. The final distillate was passed through a wet filter paper to remove any oil carried over, made up to a definite volume, and titrated for acetone by Messenger's method. The results are as follows:

MATERIAL	Acetone Per cent by weight	MATERIAL	Acetone Per cent by weight
White pine	1.76	Western larch bark	1.33
Aspen	2.19	Hydrocellulose	2.20
Yellow birch (*a*)	2.17	Oxycellulose	0.81
Yellow birch (*b*)	2.05	Starch	2.34
Hydrolyzed white pine	1.28		

The hydrocellulose was prepared by exposing cotton to the fumes of concentrated hydrochloric acid for 50 hours and washing thoroughly. The oxycellulose was prepared with nitric acid by the method of Nastjukoff.[5] The hydrolyzed wood was the residue from the semicommercial manufacture of ethyl alcohol.

It will be noted that the yield of acetone is of the order of 2 per cent; it is probable that these results are somewhat too high owing to the presence of unsaturated compounds. That acetone is formed was shown by the preparation of dibenzylidene acetone (m. p. 114° C.). Basset does not give his method of analysis, but his results are explainable on the supposition that he used the titration method on a distillate containing a large amount of unsaturated compounds. A distillate from sugar maple that was merely redistilled and filtered to remove oil showed 6 per cent of acetone. Owing to the formation of mesityl oxide by boiling acetone with calcium oxide,[6] it was possible that acetone had been lost by condensation to mesityl oxide and phorone. These higher ketones are decomposed by boiling dilute acids,[7] also by alkalies.[8] To determine this point two distillations of 50 grams of white pine with lime were made in the regular way. Sufficient dilute sulfuric acid and distilled water were added to the distillate to give a volume of 200 cc. having an acid concentration of 0.25 per cent. After refluxing 7 hours the solution was distilled, then redistilled twice after having been made slightly alkaline. The yields of acetone were 1.37 and 1.25 per cent, respectively.

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[1] Received May 23, 1925.

[2] *Chem. Met. Eng.*, **20**, 190 (1919).

[3] This Journal, **14**, 43 (1922).

[4] *Ann. chim. phys.*, [2] **59**, 5 (1835); *Ann.*, **15**, 277 (1835).

[5] *Ber.*, **34**, 3589 (1901).

[6] Hoffman, *J. Am. Chem. Soc.*, **51**, 722 (1909).

[7] Claissen, *Ann.*, **180**, 19 (1876).

[8] Harries, *Ber.*, **32**, 1328 (1899).