

it is rather uncertain in this respect. It can be kept at a moderately high temperature ( $70^{\circ}$  C.) without decomposition. At higher temperatures the nitroglycerol will partially evaporate; when slowly heated it explodes at  $204^{\circ}$  C. If however it contains as much as ten per cent. of camphor it burns without exploding. According to Berthelot,<sup>1</sup> gelatine composed of 91.6 per cent. nitroglycerol and 8.4 per cent. of nitro-cellulose, which are proportions corresponding to total combustion, produces by explosion  $177\text{CO}_2 + 143\text{H}_2\text{O} + 8\text{N}_2$ .

He takes  $\text{C}_{24}\text{H}_{22}(\text{NO}_3\text{H})_9\text{O}_{11}$  as the formula of the nitro-cellulose, and  $51\text{C}_3\text{H}_2(\text{NO}_2\text{H})_3 + \text{C}_{24}\text{H}_{22}(\text{NO}_3\text{H})_9\text{O}_{11}$  as the formula of the gelatine itself, its equivalent weight being 12360 grams. The heat liberated by its explosion is equal to 19381 calories, or for one kilo., 1535 calories, volume of gases reduced temperature equals 8950 liters. The relative value<sup>2</sup> of blasting gelatine to nitroglycerol is as 1.4 to 1.45, Kieselguhr dynamite being taken as 1.0. Experiments made in lead cylinders gave the relative value of

Dynamite .....	1.0
Blasting gelatine .....	1.4
Nitroglycerol .....	1.4

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## NOTES ON LÖWENTHAL'S METHOD FOR THE DETERMINATION OF TANNIN.

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THE determination of tannin is a difficult chemical problem, and to meet this difficulty, no less than sixty methods and modifications have been proposed. As early as 1870, Dr. Günther, in the *Chemical News*, said that "none of the different methods for the determination of tannin answer the purpose equally well; that is, a method that yields excellent results for the tannin in nut-galls is not applicable to the tannin in sumac."

<sup>1</sup> Explosives and Their Power, M. Berthelot.

<sup>2</sup> Messrs. Roux and Sarran.

Nearly all of these various tannin methods in principle follow one of four or five main lines: (1) The tannin is precipitated and determined as metallic tannates; (2) it is precipitated with hide powder and the tannin determined indirectly from the difference between the density of the solution before and after the precipitation; (3) it is determined colorimetrically or (4) by oxidation methods such as the Löwenthal.

The Löwenthal method is generally considered the most reliable, and is unquestionably the best method for commercial purposes. No attempt is made in these notes to compare the various tannin methods and discuss their merits or demerits, but simply to record some of the difficulties that are usually experienced in becoming acquainted with the Löwenthal method. Full directions and all of the details of the method are given in the last editions of both Sutton and Allen, but the various pitfalls in the workings of the method are not sufficiently noted.

In order to facilitate matters a brief outline of the method is given. The solutions and reagents employed are: (1) A standard solution of potassium permanganate; (2) a standard solution of indigo sulphate; (3) dilute sulphuric acid 1 : 4; (4) a solution of gelatine, twenty-five grams per liter.

The permanganate oxidizes the indigo, tannin, and all other organic matters that are present and are oxidized under the conditions of the titration. Let this amount of permanganate be denoted by  $a$ . The indigo is employed as an indicator, and is titrated against the permanganate either before or after each determination, and the solution is usually of such a strength that ten cc. is equivalent to five cc. of the permanganate; let this factor be denoted by  $b$ . The tannin is removed by precipitation with gelatine, and the soluble non-tannin organic matters oxidized by the permanganate; let this amount be denoted by  $c$ ; then  $(a-b) - (c-b) = x$ ,—the amount of permanganate necessary to oxidize the tannin, from which the equivalent amount of tannic acid is determined. The value of  $x$ , it will be seen, depends upon the accuracy of at least three permanganate titrations upon an unknown number of organic compounds, all capable of reacting differently with the permanganate under different conditions.

The main points to be observed are: (1) The care and prepar-

tion of the gelatine solution; (2) the titration of the non-tannin materials; (3) and the end point of the reaction.

The gelatine solution should be sterilized otherwise the solution frequently becomesropy and liquid in a short time, on account of the action of micro-organisms. Blank determinations should be made with the gelatine, and corrections made for all oxidizable materials that it may contain and give up to the filtrate. Frequently the results are too low on account of too large a factor being deducted for the non-tannin materials, when a small portion is due to the gelatine. Qualitative tests should also be made to determine whether or not the tannin has been completely precipitated. A hot filtration funnel can be employed to advantage, and the gelatinous precipitate washed by decantation until no qualitative test can be obtained for tannin.

The oxidation of the non-tannin materials is one of the chief causes of trouble, and since these compounds are present in both initial and subsequent titrations, great care should be taken to have all of the conditions the same throughout the entire process. As in the oxidation of organic matter by permanganate in water analysis, the degree of oxidation is proportional to the length of time allowed for the action of the permanganate, as well as to the temperature employed for the reactions. Should the first titration be carried on at a higher temperature or require a longer period than the second titration, the factor for the non-tannin materials would be a variable, and the results would be that the tannin factor would also be a variable. This source of error can be brought under control by strict uniformity in each operation.

The end reaction is quite marked, and after some acquaintance with the titration it can be predicted from the intermediate changes of color. The color of the solution at first is dark blue. The permanganate can be run in, drop by drop, until the color changes to a faint blue tint; the cautious addition of only a few drops more will produce the desired yellow tinged solution with a pink shaded ring around the edge of the porcelain dish. Should this point be passed, one or two cc. of the indigo solution can be added, and the titration completed. In the calculation of the results make the necessary corrections for all indigo so used.

It is advisable at the outset to become acquainted with the workings of the method, using a good commercial sample of tannic acid, before attempting to determine the tannin in oak bark, tea, or other tannin yielding materials.

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## THE CHEMICAL INDUSTRY OF THE UNITED STATES.

BY HENRY BOWER.

THE chemical industry of the United States, in common with the other leading branches of manufactures, shows a remarkable increase in the decade between 1880 and 1890, and this is accompanied, in some instances, by results of such magnitude as to become phenomenal.

TOTALS OF PRODUCTIONS OF CHEMICALS IN THE UNITED STATES IN 1890.

	Value.
Alum (94,174,008 lbs.) .....	\$1,625,210
Coal tar products .....	687,591
Dyeing and tanning extracts and sumac.....	7,947,841
Gunpowder and explosives (108,735,980 lbs.)....	10,802,131
Fertilizers (1,818,552 tons) .....	34,038,452
Paints, white and red lead colors, and varnishes	52,434,690
Pharmaceutical preparations.....	16,486,643
Potash and pearlash (4,874,439 lbs.).....	185,247
Sodas (329,369,633 lbs.) .....	5,384,400
Sulphuric acid.....	6,522,591
Wood alcohol and acetate of lime.....	1,885,469
Chemicals, including all acids, bases, and salts not heretofore enumerated.....	25,140,425
All other products.....	12,903,943
	\$176,044,633

*Sulphuric Acid.*—The most important of all chemical manufactures is sulphuric acid, which maintains its supremacy over any other known article in promoting the manufacturing interests of the world. The large increase in the number of establishments and in the quantity produced indicates the advance that has been made in general manufactures in the United States during the last decade.

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893.