

NOTE ON THE ESTIMATION OF TANNIC AND GALLIC ACIDS.

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Since 1799, numerous methods have been suggested for the estimation of tannic and gallic acids, but most of them are highly erroneous as admitted by the authors. The methods in common use may be classified under (1) Oxidation, (2) Adsorption, (3) Precipitation by metallic salts, (4) Precipitation by alkaloids, and (5) Iodination.

(1) *Oxidation*.—The methods of Lowenthal (*J. pr. Chem.*, 1863, 3, 150) and Thompson (*Chem. Zentr.*, 1902, 2, 1395) were tried for the estimation of tannins in tan-liquors; the former was found to be highly tedious and the latter did not give consistent results.

(2) *Adsorption*.—These methods, though commonly adopted in tanneries, were found to be erroneous. A similar observation has been made by Dreaper (*Chem. News*, 1904, 90, 111).

(3) *Precipitation by metallic salts*.—Most of the methods were found to be unsatisfactory. The method of Dreaper (*loc. cit.*) was found to be reliable only when the concentration of tannic acid was high.

(4) *Precipitation by alkaloids*.—Rather low values for pure tannic acid were obtained by the strychnine method of Trotman (*Analyst*, 1906, 31, 53). The cinchonine method of Ostermayer (*Chem. News*, 40, 181) was also found to be unsatisfactory for the same reason.

(5) *Iodination*.—The method of Ferdinand (*Chem. Zentr.*, 1900, 1, 1107) when tried for the estimation of pure tannic acid, did not yield consistent results. Boudet's modification (*Bull. Soc. Chim.*, 1906, 35, 760) of the above method was also found to be defective because the reaction was not complete at the end of 2 hours as suggested by the author. Tables I and II give the amounts of iodine ($N/100$) taken up at different intervals, by 5 c.c. each of a 0.225 per cent. solution of tannic acid and a 0.0955 per cent. solution of gallic acid respectively.

The method of Gardner and Hodgson (*J.C.S.*, 1909, 95, 1819) was next tried. Fairly accurate and concordant results were obtained for tannic and gallic acids, at different concentrations, both singly and mixed. In adopting the above method, it was found advantageous to

TABLE I.

Time in hours	0	2	4	6	8	11
Iodine, c.c. N/100 absorbed	18.7	22.1	22.6	23.0	23.3	23.8

TABLE II.

Time in hours	0	12	17	42	90
Iodine, c.c. N/100 absorbed	18.5	24.0	26.9	28.3	29.6

precipitate tannic acid with a mixture of gelatin and acid sodium chloride as suggested by Lowenthal (*loc. cit.*) rather than with gelatin alone.

Minute quantities of iodine were found to be adsorbed by the gelatin remaining in solution after the removal of tannic acid. This defect was overcome by carrying out a blank with gelatin alone and applying the necessary correction.

Aqueous solutions (0.1 per cent.) of tannic and gallic acids were mixed in different proportions and estimated by the modified method of Gardner and Hodgson (*loc. cit.*). The results which have been given in Table III show that accurate and concordant results can thus be obtained.

TABLE III.

Mg., actually present, of		Iodine (N/10) required for the mixture	Iodine (N/10) required for gallic acid only	Mg., as calculated, of	
Tannic acid	Gallic acid			Tannic acid	Gallic acid
10	...	4.7	...	10.0	0.0
8	2	4.9	1.1	8.0	2.1
6	4	5.0	2.2	6.0	4.1
5	5	5.1	2.7	5.1	5.0
2	8	5.2	4.2	2.0	7.9
0	10	5.3	...	0.0	10.0

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In the course of the foregoing series of determinations, it was also observed that the reaction of the mixture became more acid as the concentration of gallic acid increased. With a view to ascertaining whether, by measuring the reaction, the proportions in which the two acids occur can be determined, tannic and gallic acids (0.4 per cent. each) were mixed in different proportions and the hydrogen-ion concentrations of the mixtures determined electrometrically (Table IV).

TABLE IV.

Percentages			Percentages		
Tannic acid	Gallic acid	P _H	Tannic acid	Gallic acid	P _H
100	0	3.7	60	40	3.26
95	5	3.58	55	45	3.23
90	10	3.55	50	50	3.20
85	15	3.48	45	55	3.19
80	20	3.40	40	60	3.15
75	25	3.36	35	65	3.10
70	30	3.32	30	70	3.08
65	35	3.28

As may be seen from the above, the differences in reaction are not so distinct as to warrant an extensive application of the method, particularly to vegetable extracts which contain large amounts of buffering materials.

SUMMARY.

A number of methods were tried for the estimation of tannic and gallic acids both singly and together. Among them, the method of Gardner and Hodgson (*J.C.S.*, 1909, **95**, 1819) with a slight modification was found to be the most reliable.

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