

CCXXIV. DETERMINATION OF THE FURFURALDEHYDE YIELD OF SOILS AND OF PLANT MATERIALS ADMIXED WITH SOIL

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THE procedure usually employed for the estimation of the furfuraldehyde yield of plant materials is the phloroglucinol method of Kröber [A.O.A.C. 1935], but this method is time-consuming and the materials required are rather costly. Powell & Whittaker [1924] recommended the bromine titration method as giving consistent results which agreed with those obtained by the phloroglucinol procedure. The bromine method takes a much shorter time (about an hour) and the materials required are more easily available.

A preliminary comparison of the two methods showed that the bromine method gave good agreement with the phloroglucinol procedure for plant materials (Table I).

Table I. *Furfuraldehyde yield from plant materials*

Plant material	Amount taken mg.	Furfuraldehyde yield by	
		Bromine titration mg.	Phloroglucinol precipitation mg.
(1) Rice straw	400	53.2	52.1
(2) Oat straw	300	49.4	48.7
(3) Barley straw	300	49.8	49.1
(4) Ragi straw	300	54.1	53.2
(5) Grass (lawn mowings)	500	38.4	37.6
(6) Bracken leaves	1000	42.2	41.1

An examination of the applicability of either method to soils and materials admixed with soil raised several difficulties. The first lay in the procedure for distillation itself. It was found highly inconvenient to follow Kröber's procedure of adding 30 ml. portions of 12% HCl every 10 min. directly to the distilling flask, on account of the excessive bumping of the soil mass. This was avoided by taking 700 ml. of 12% HCl in a conical flask and distilling it into a 300 ml. distilling flask containing the soil material mixed with 50 ml. of 12% HCl, at such a rate that 500 ml. were collected in 2½ hr. This volume of distillate was found sufficient to collect almost the whole of the total furfuraldehyde yield obtainable from the material concerned.

The second difficulty met with was the adverse effect of the presence of soil on the yield of furfuraldehyde obtained. Considerably lower values were obtained in most cases (*vide* Table II) in presence of soil than in its absence, as has already been reported elsewhere [Acharya, 1937].

Table II. *Influence of soil on the estimation of furfuraldehyde yield*

Soil added	Furfuraldehyde yield in mg. (values for the soils only have been deducted in each case)		
	Rice straw 0.4 g.	Wheat straw 0.4 g.	Barley straw 0.4 g.
(1) Control value without the addition of soil	55.2	69.6	65.4
(2) 5 g. Paddy soil from Aduturai (India)	38.4	52.8	49.2
Do. ignited	32.4	46.2	43.8
(3) 5 g. Paddy soil from Coimbatore (India)	43.2	58.2	54.0
Do. ignited	36.6	52.2	47.6
(4) 5 g. Woburn soil (sandy loam) (England)	52.2	66.0	62.4
Do. ignited	45.6	59.4	56.4
(5) 5 g. Woking soil (sand)	55.2	69.6	65.4
Do. ignited	55.2	69.6	65.4

The results presented in Table II are typical of those obtained by an examination of a large number of soil samples. Heavy soils generally showed a greater interfering effect in the estimation of furfuraldehyde than light and sandy soils, and the adverse effect increased with the proportion of soil to plant material taken. This interfering effect was not due to the organic matter fraction of the soil (e.g. lignin), as shown by the fact that ignition of the soil not only failed to remove, but increased the harmful effect.

A detailed examination of the nature of the interference of soil in the estimation showed it to be due to the presence of oxidizing compounds in the soil, e.g. ferric and manganese compounds and nitrate (*vide* Table III). Bengtsson [1936] has noticed that in presence of nitrate lower values are obtained for furfuraldehyde and has recommended that in such cases the material should be washed with water to remove the nitrate before distilling for furfuraldehyde. Such a treatment, however, when applied to the soils examined, instead of improving the recovery of furfuraldehyde, actually tended to lower it, showing that the oxidizing action of soil is due only in minor degree to the nitrate content, but is brought about mainly by the inorganic mineral constituents, such as ferric and manganese compounds.

Table III. *Influence of oxidizing agents on the recovery of furfuraldehyde*

Substance added	Furfuraldehyde yield in mg.		
	Furfur- aldehyde solution	Rice straw 0.4 g.	5 g. Aduturai soil and 0.4 g. of rice straw
(1) Control value without any addition	60.6	68.4	52.8
(2) Ferrous sulphate, 1 g.	60.6	68.4	52.8
(3) Ferric alum, 1 g.	58.2	57.0	46.2
(4) Ferric chloride, 1 g.	56.4	40.2	36.0
(5) Ferric oxide, 1 g.	55.2	24.0	22.8
(6) Manganous chloride, 1 g.	60.6	68.4	52.8
(7) Manganese dioxide, 1 g.	Nil	9.0	8.6
(8) Sodium nitrate, 1.2 mg.	58.2	65.4	49.2

As the removal of the interfering constituents could not be effected by water, an attempt was made to reduce the compounds. Various reducing agents such as Sn and HCl, Zn and HCl, Devarda's alloy in alkaline medium were tried, but the best was found to be the addition of stannous chloride (10% solution in HCl). This was therefore added to the soil in all distillations, and a comparison of the bromine titration and phloroglucinol methods was made.

Table IV gives the influence of adding different amounts of stannous chloride on the yield of "apparent furfuraldehyde", as determined by the two methods. The figures show that whereas the bromine value increases rapidly with increasing amounts of stannous chloride added, the phloroglucinol value first rises to a steady level and then shows an actual decrease. That the increase in bromine value was not due to a portion of the added stannous chloride being carried over with steam into the distillate was shown by running suitable blanks.

Table IV. *Influence of the amount of stannous chloride added on the recovery of furfuraldehyde from soils*

Amount of stannous chloride added	Furfuraldehyde yield by		
	Bromine titration method mg.	Phloroglucinol method	
		Before alcohol treatment mg.	After alcohol treatment mg.
(1) Rice straw, 0.4 g. only	53.2	52.1	51.8
(2) Aduturai soil, 5 g. and 0.4 g. rice straw, without stannous chloride	35.3	34.7	34.2
(3) Do. with 5 ml. SnCl ₂	53.6	52.8	52.1
(4) Do. with 10 ml. SnCl ₂	58.1	52.2	51.0
(5) Do. with 15 ml. SnCl ₂	62.6	46.4	40.1
(6) Do. with 25 ml. SnCl ₂	67.2	38.2	26.5
(7) Blank with 25 ml. SnCl ₂ only without added material	Nil	Nil	Nil

The increasing solubility of the phloroglucinol precipitate in alcohol, at higher concentrations of stannous chloride, suggested the formation of methylfurfuraldehyde under these conditions [cf. Fenton & Gostling, 1901]. An examination of the behaviour of non-pentose carbohydrates such as glucose, starch and cellulose in presence of stannous chloride confirmed this view (Table V). Apparently, in the case of straw, the excess of stannous chloride should have similarly interacted with the non-pentose materials therein. Methylfurfuraldehyde combines with bromine similarly to furfuraldehyde, and it is difficult to distinguish between the two or to determine their relative proportions by this method. With phloroglucinol, however, methylfurfuraldehyde is partially precipitated as a brown precipitate which is readily soluble in hot alcohol. It is therefore possible to separate the two compounds and obtain correct values for furfuraldehyde only by treating the combined precipitates with boiling alcohol.

Table V. *Influence of SnCl₂ on the distillation of non-pentose materials with 12% HCl*

Added 10 ml. of 10% SnCl ₂ and distilled. Controls without SnCl ₂ deducted in each case	Apparent furfuraldehyde yield by		
	Bromine titration method mg.	Phloroglucinol method	
		Before alcohol treatment mg.	After alcohol treatment mg.
(1) Glucose, 1 g.	48.4	35.3	Nil
(2) Soluble starch, 0.5 g.	44.1	33.7	Nil
(3) Filter paper, 1 g.	22.2	15.1	Nil
(4) Oat straw cellulose, 0.5 g.	31.4	23.2	Nil
(5) Lignin, 0.5 g.	Nil	Nil	Nil

When there is only a slight excess of stannous chloride present beyond what is necessary to reduce the oxidizing substances contained in the soil sample taken, the bromine and phloroglucinol methods give concordant results. With larger amounts of stannous chloride up to nearly twice the required amount, the phloroglucinol value remains stationary while the bromine value steadily increases and the distillate becomes coloured yellow (*v.* Table IV). This difference between the two methods is apparently due to the fact that within this range the amount of methylfurfuraldehyde formed is comparatively small (about 10% of the furfuraldehyde produced) and is but partially precipitated by phloroglucinol. Even the small amount that may be so precipitated can be removed by treatment with boiling alcohol. With larger amounts than double the required quantity, however, the effect of stannous chloride is to depress the amount of furfuraldehyde formed and increase that of methylfurfuraldehyde and its volatile decomposition products. Hence the bromine value continues to increase, while the phloroglucinol value decreases, and the residue after alcohol treatment shows a still more rapid decrease.

Usually, a quantity of 10% SnCl_2 corresponding to 1 ml. per g. of soil taken is found to be a good approximation to the quantity required for reduction of oxidizing substances present; and the distillates obtained are colourless. Sandy soils require rather less, whilst clayey soils require relatively more. As it is difficult, however, to judge beforehand the exact amount of SnCl_2 to be added in each case, and a slight excess vitiates the bromine value, but does not affect the phloroglucinol value, it is concluded that for soils and plant residues mixed with soil, distillation of the material with 12% HCl in presence of stannous chloride and estimation of the furfuraldehyde evolved by precipitation with phloroglucinol, followed by extraction of the precipitate with boiling alcohol, is preferable to the bromine titration method of Powell & Whittaker [1924].

SUMMARY

1. The present paper reports a comparison of the bromine titration method of Powell & Whittaker and the gravimetric phloroglucinol method for the estimation of the total furfuraldehyde yield of soils and plant materials admixed with soil. In the absence of soil, the two methods were found to give concordant results.

2. In presence of soil, however, low results were obtained by both the methods, owing to the presence of oxidizing agents such as ferric and manganese compounds and nitrate in the soil, which apparently oxidize a portion of the furfuraldehyde during the course of distillation with 12% HCl. The addition of stannous chloride in regulated amounts serves to reduce such oxidizing agents and yield the proper recovery of furfuraldehyde. About 1 ml. of 10% SnCl_2 per g. of soil was found to be sufficient for most soils and to leave a slight excess.

3. This excess of stannous chloride, however, tends to produce methylfurfuraldehyde, which reacts with bromine and increases the "apparent" furfuraldehyde yield as determined by bromine titration. The interference is much less in the case of phloroglucinol, as methylfurfuraldehyde is only partially precipitated by this reagent and even this interference can be removed by treating the combined precipitate with boiling alcohol, in which the impurity is easily soluble. A large excess of stannous chloride, however, gives a coloured distillate and depresses the formation of furfuraldehyde.

4. Hence, it is concluded that for soils and plant materials mixed with soil, distillation of the material with 12% HCl in presence of stannous chloride and

estimation of the furfuraldehyde by precipitation with phloroglucinol, followed by extraction of the precipitate with boiling alcohol, is preferable to the bromine titration method of Powell & Whittaker.

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