

The Estimation of Furfural, Extract, Permanganate Time and pH in Beverage Spirits

Fifth Report of the Research Committee on the Analysis of Potable Spirits

Methods for the estimation of furfural and extract in whiskies, rums and brandies are reviewed and procedures are recommended as a result of inter-laboratory studies.

Methods for permanganate time and pH for use on alcohol intended for the production of gin or vodka have also been investigated by limited studies. No method for permanganate time can be recommended except for the limited purposes of internal manufacturing control.

Previous reports of the Committee discussed the estimation of higher alcohols¹, methanol², esters, aldehydes and total acidity³ and the determination of strength⁴. In continuation of this work we now report on methods for furfural and extract in spirits and for permanganate time and pH of highly rectified spirits for beverage uses. No difficulty was found in selecting satisfactory methods for extract and pH but serious flaws have been discovered in a method widely used for furfural and in the internationally accepted method for permanganate time.

Furfural in Plain Spirits (e.g. Whisky)

Published methods for estimation of furfural in spirits include the following.

- A. Steam distillation of the sample followed by measurement of the ultra-violet absorption of the distillate. This is the official method of the Association of Official Analytical Chemists⁵.
- B. Measurement of the pink colour produced in a sample distillate by aniline acetate solution. This is the official French method⁶.
- C. Gas liquid chromatography⁷.
- D. Polarography⁸.

Method B has been compared with method A and gives a result which is up to 30 per cent. less⁹; and with method D, giving a result up to 50 per cent. less⁸. Methods A and D are reported to agree⁸. No comparison of any gas liquid chromatographic (GLC) method with methods A, B or D appears to have been made prior to that reported in Table I, in which a number of GLC procedures have been compared with the results obtained by the AOAC ultraviolet spectrophotometric method. This shows that method A gives a higher result than method C, also to the extent of about 50 per cent. on average.

TABLE I
COMPARISON OF GLC PROCEDURES AND U.V. SPECTROPHOTOMETRY
FOR ESTIMATION OF FURFURAL IN BEVERAGE SPIRITS
grams of furfural per 100 litres of ethanol

Sample	u.v.	GLC
Furfural in ethanol	0.26	0.27
Scotch grain whisky (a)	0.18	0.15
Blended Scotch whisky (b)	1.27	1.06
	1.63	1.06
	2.08	1.41
Scotch malt whisky (c)	3.14	2.32
Rum	1.60	0.70
Rum (d)	3.23	2.53
Brandy (e)	1.32	0.96
Brandy	1.90	1.20
Brandy	3.59	2.94

The tabulated values are the mean of results obtained in at least six independent laboratories. Samples (a) to (e) are correspondingly labelled in Table IV.

As far as is known the aniline acetate method is specific for furfural¹⁰ and GLC should also be specific, provided that the internal standard and furfural are adequately resolved from other constituents. Thus, the commonly used ultra-violet absorption method must be suspected of giving a substantial systematic error.

The ultra-violet absorption spectrum of furfural is not particularly characteristic and any other aldehydes and ketones also present in a sample might well contribute to the absorbance measured in method A. To assess whether this might be significant, a grappa brandy containing a total of 233 g of aldehyde per 100 l ethanol, expressed as acetaldehyde, was analysed by methods A, B and C with the results given in Table II. This brandy was also distilled and then fractionally distilled with the results shown in Table III.

TABLE II
FURFURAL IN GRAPPA BRANDY AS ESTIMATED BY DIFFERENT METHODS

Method	<i>g of furfural per 100 l of ethanol</i>
A. Ultra-violet spectrophotometry	1.38
B. Aniline acetate colorimetry	0.60
C. Gas liquid chromatography	0.65

TABLE III
"FURFURAL" IN FRACTIONS OF GRAPPA DISTILLATE AS
ESTIMATED BY THE U.V. METHOD

Distillation range	<i>g of "furfural" per 100 l of ethanol</i>
(i) Below 77°C	0.07
(ii) 77–78°C	0.00
(iii) 78–98°C	0.85
(iv) Column hold-up and not distilled	0.56

The u.v. absorption spectra of fractions (iii) and (iv) show that substantial amounts of u.v. absorbing materials other than furfural are present. Because of its boiling range fraction (i) is not likely to contain furfural.

It is considered that the possible error in the estimation of furfural by method A makes the method unsatisfactory for use in analysis of beverage spirits and the ultra-violet spectrophotometric method is therefore not recommended. Method B is sensitive to temperature, acidity, reagent concentration and alcohol concentration, which affect the rate of development and loss of the coloured compound¹¹. In addition aniline presents a toxic hazard. For these reasons we undertook no further studies.

GAS LIQUID CHROMATOGRAPHIC METHODS

The GLC results of Table I are means of values obtained by several laboratories using different stationary phases and temperature programmes. Individual results are not reported but the variation is similar to that recorded in Table IV.

TABLE IV
FURFURAL IN BEVERAGE SPIRITS, GLC METHOD
grams per 100 litres ethanol

	Grain whisky (a)	Blended whisky (b)	Malt whisky (c)	Light rum	Rum (d)	Brandy (e)	Brandy
Analyst							
1	0.12	1.05	2.48	0.16	2.88	1.09	2.65
2	0.14	0.96	2.06	0.13	2.42	0.86	2.50
3	0.16	1.05	2.49	0.25	2.53	1.02	3.80
4	0.24	1.10	2.50	0.16	2.70	1.20	3.16
5	—	0.95	2.30	0.21	2.58	0.70	3.00
6	0.15	1.50	2.30	—	—	—	3.16
7	0.11	0.79	2.09	0.16	2.06	0.90	2.86
Mean	0.15	1.06	2.32	0.18	2.53	0.96	3.02
Standard deviation	0.95	0.22	0.19	0.94	0.28	0.18	0.42
100 s.d./mean	30	21	8	24	11	19	14

Samples (a) to (e) are correspondingly labelled in Table I.

The data of Table IV were obtained using 15 per cent. Carbowax 1540 on 80–100 mesh Chromosorb W-AW DCMS in 1.8 m × 6 mm OD columns. The

column was usually operated at 112°C for 4 minutes and then heated to 152°C at 2°C/min. It is essential to avoid the production of interfering material by pyrolysis of the extract and, if an on-column injection technique is not used, the temperature of the injector must be such that this does not occur, i.e. less than about 130°C. Some analysts used the column isothermally but all used conditions such that furfural was resolved from ethyl octanoate and from *iso*amyl hexanoate. Heptan-1-ol and octan-1-ol are satisfactory internal standards.

It has been found that substantial errors can be introduced by the use of manual methods of measuring the detector response. When very small responses are involved, an integrator properly set up is likely to give a more accurate measurement than any manual assessment. Although no collaborative testing using electronic integrators has been carried out, the experience of individual laboratories indicates that such an instrument should be used if possible. If an integrator is not available, the most reproducible results are obtained by choosing chromatographic conditions giving "sharp" peaks with satisfactory resolution of the constituents of interest. Peak height measurements are then appropriate.

The GLC method described has proved adequate in members' hands but, provided that good separation of furfural and the internal standard from all other components is achieved, satisfactory results should be obtained by competent laboratory staff regardless of the type of column packing material used.

A GLC procedure is therefore recommended as more specific and accurate for the estimation of furfural than the ultra-violet spectrophotometric method.

Extract in Plain Spirits (e.g. Whisky)

Published methods for the determination of extract are as follows.

(A) Association of Official Analytical Chemists (AOAC)¹². "Weigh or measure at 20°C, 25–100 ml of sample, evaporate to dryness on a steam bath, dry 30 minutes at 100°C, cool in a desiccator for 30 minutes and weigh." This method is unchanged from the first edition of AOAC methods, 1916, except that the drying time has been decreased at various times from 2.5 hours to 0.5 hours. There has been no published discussion of the changes and no collaborative work is known.

(B) The official French method¹³. "25 cm³ of spirit is placed in a previously weighed cylindrical dish with a flat bottom 55 mm in diameter. During the first hour of evaporation the dish is placed on the corner of a steam bath in such a way that the liquid does not boil, which could provoke losses by spitting. The drying is completed by placing the dish on an opening of the steam bath for two hours. The dish is cooled in a desiccator and reweighed." This method does not appear to have been evaluated by collaborative tests, though as a means of obtaining obscuration of spirits it has been compared with a specific gravity method¹⁴.

The AOAC method was selected for study because special apparatus is not required. Each analyst made a single determination on each sample. The results at Table V show that the method can be recommended.

TABLE V
COLLABORATIVE STUDY OF EXTRACT IN SPIRITS
grams of extract per 100 millilitres of spirits

	Whisky	Rum	Whisky†	Brandy
Analyst 1	0.092	0.150	0.623	0.961
2	0.115‡	0.160	0.625	0.891
3	0.088	0.157	0.625	0.920
4	0.089	—	0.616	—
5	0.079	0.150	0.596	0.900
6	0.088	—	0.567	—
7	0.098	0.160	0.630	0.903
8	0.095	0.173‡	0.625	0.935
9	0.100	0.154	0.680‡	0.962
Mean	0.094	0.158	0.621	0.925
Standard deviation	0.010	0.008	0.030	0.029
100 s.D./mean	11	5.0	4.8	3.1

†Caramel added.

‡Possible outlier at 10 per cent. significance level.

Permanganate Time of Alcohol for Compounded Spirits

Permanganate time is regarded as a measure of oxidisable impurities in alcohol of high quality such as is used in the manufacture of gin or vodka. It is the time required to reduce the colour of permanganate added to the sample to a standard colour, or to remove it completely. Alternatively it is used as a limit test in which colour must remain after a certain interval of time. Some of the details specified for this method by various authorities are listed in Table VI, which is not a full compilation.

None of these variants appears to have been evaluated by collaborative test, though permanganate time is a frequent item in specifications. The ISO method¹⁵ was chosen for study as having probably the widest acceptance. Samples of fermentation alcohol were packed in glass bottles with foil caps and stored cool and in the dark until they were analysed by participating laboratories on as nearly as possible the same day. The results of this test are collated in Table VII.

Some analysts found that the reference colour did not match the colour of the test solutions near the end-points; and it was often difficult to maintain the temperature of the test solution within the specified band. Most preferred to view down the axes of the sample cylinders. Absorption spectra of permanganate, of permanganate partly reduced under the conditions of the test, and of the reference solution are shown in Figure 1.

The difficulty of comparing colours which are not quite the same in hue is thought to be the main cause of the discrepancies between laboratories. Permanganate times measured in individual laboratories appear to be reproducible; nevertheless the data of Table VII shows that different laboratories may well

TABLE VI
COMPARISON OF STANDARD METHODS FOR PERMANGANATE TIME

Authority	Temperature, °C	Permanganate concentration, g/l of sample	Volume of reagent, ml	Volume of sample, ml	Water added by reagent, per cent.	Standard Colour Solution	Viewing axis	Specified time, min.	Notes
BS 506: 1966 ASTM D 1363-67	15.5 ± 0.5 15.5 ± 0.5	0.0080 0.0080	2.0 2.6	50 50	4.0 4.0	0.5% CoCl ₂ ; 0.56% UO ₂ (NO ₃) ₂ As above	Horizontal Vertical	—†	The only method to state that the colour standard is stable
ISO 1971	15 ± 0.2	0.0040	1.0	50	2.0	0.25% CoCl ₂ ; 0.28% UO ₂ (NO ₃) ₂ ; 10% of 2N HNO ₃	Horizontal	—†	
Swiss Monopoly	15	0.0040	1.0	50	2.0	As above	N.S.	—†	
Polish Monopoly	15	0.0040	1.0	50	2.0	As above	Horizontal	—†	
U.S. Pharm.	15	0.0158	0.1	20	0.5	None	N.S.	5†	End point—pink colour
U.S. Nat. Form.	15	0.0158	0.1	20	0.5	None	N.S.	5†	Does not disappear
ACS 1960	15	0.0158	0.1	20	0.5	None	N.S.	5†	
French Pharm. 1968	15-18	0.016	2.0	25	8.0	None	N.S.	20	End point—salmon pink. Sample from 1st 30 ml of 50 ml distillation
B. Pharm. 1973	20	0.0158	1.0	20	5.0	None	N.S.	10	End point—when colour discharged
German Pharm. 1968	20 ± 1	0.3161	1.0	10	10.0	0.5% FeCl ₃ ; 1.7% CoCl ₂ ; 0.63% HCl	N.S.	10†	Temp. adjusted after mixing
German Monopoly	20	0.3161	1.0	10	10.0	Available from Monopoly	N.S.	—†	End point—salmon pink
Internat Pharm.	20	0.100	1.0	10	10.0	None	N.S.	10†	End point—not brown

N.S. = not specified.

†Time depends on the grade specified.

be in serious disagreement. It is considered that the test is suitable only for manufacturers' and traders' internal quality control purposes.

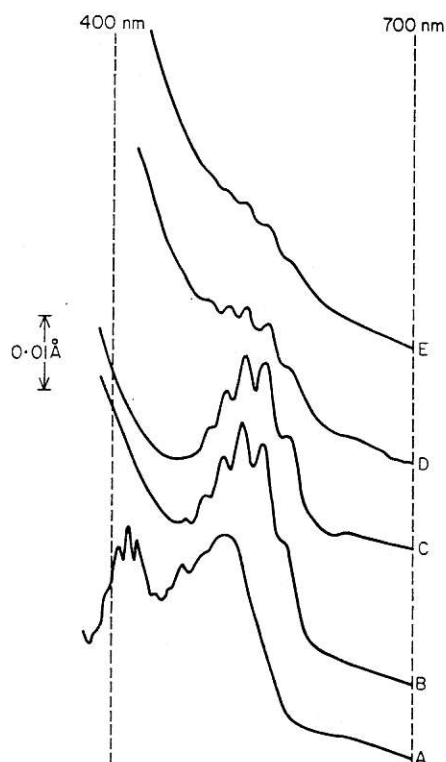


Fig. 1. Optical density of solutions used in permanganate test vs. water; 1 cm cells. A, ISO colour standard; B, dilute permanganate; C, test after 5 minutes; D, test at end-point (15 minutes); E, test beyond end-point.

TABLE VII
PERMANGANATE TIME BY THE ISO METHOD
minutes

Analyst	Sample					
	1	2	3	4	5	6
1	41	30	26	29	17	13
2	46	37	33	27	17	20
3	34	24.5	23	24	13.5	14.5
4	30	25	22	20	17	14
5	38	35	32	30	18	16
6	39	32	31	31	22	19
7	39	35	38	36	18	21
8	37	43	37	36	21	18
9	40	24	24	20	12	13
10	—	29	28	19	20	16

pH of Highly Rectified Spirit

The measurement of pH is primarily of interest for quality control purposes in manufacture, transport or storage.

APPARATUS

pH meter with calomel and glass electrodes.

METHOD

Dilute the sample to approximately 40 per cent. v/v strength, using freshly boiled and cooled distilled water. Measure the pH according to the instrument instructions, allowing a steady state to be reached.

In collaborative test the values recorded in Table VIII were obtained and indicate the agreement which may be expected between laboratories.

TABLE VIII
pH VALUE OF RECTIFIED SPIRIT

Analyst pH	1	2	3	4	5	6	7	8	9
	7.1	6.6	6.8	5.8	6.8	6.6	6.2	6.5	6.5

Carbon dioxide absorption could give rise to pH values as low as 5.5 in rectified spirit. pH is not likely to be a primary cause of dispute but can be indicative of some contamination which would require investigation.

References

1. First Report of the Research Committee on the Analysis of Potable Spirits, *J. Assoc. Publ. Analysts*, 1970, **8**, 81.
2. Second Report, *ibid.*, 1972, **10**, 49.
3. Third Report, *ibid.*, 1974, **12**, 40.
4. Fourth Report, *ibid.*, 1974, **12**, 45.
5. "Methods of the Association of Official Analytical Chemists", 12th Edn., Washington, D.C., 1975, 9.081-9.082.
6. "Textes d'Intérêt Général", 73-231, p. 22.
7. Duncan, R. E. B., and Philp, J. M., *J. Sci. Food Agric.*, 1966, **17**, 208.
8. Mofidi, J., *et al.*, *J. Food Sci.*, 1976, **41**, 471-473.
9. Schoenman, R. L., *J. Assoc. Off. Agric. Chem.*, 1960, **43**, 657.
10. Harrison, R. B., *et al.*, *Analyst*, 1961, **86**, 561.
11. Stillings, R. A., and Browning, B. L., *Ind. Eng. Chem. Anal.*, 1940, **12**, 499.
12. "Methods of the Association of Official Analytical Chemists", 12th Edn., Washington, D.C., 1975, 9.022.
13. "Textes d'Intérêt Général", No. 73-231, pp. 10-11.
14. Wagstaff, P. J., *Analyst*, 1976, **101**, 292.
15. "Determination of permanganate time". ISO/R 1388-1970E.