

The Analysis of Potable Spirits

Second Report of the Research Committee on the Analysis of Potable Spirits: The Estimation of Methanol in Potable Spirits

The First Report of the Committee¹ gave its terms of reference and membership and described approved methods for the estimation of the higher alcohols in spirits. The gas liquid chromatographic methods detailed are also suitable for the estimation of methanol and some results obtained by their use are now reported. A rapid GLC method is also described for use when only the methanol content of a sample is required, together with a colorimetric procedure based on a method by Mathers^{2,3}.

A. COLORIMETRIC METHOD

Principle

The methanol is separated from most of the ethanol by fractional distillation. The methanol is then oxidised by acid permanganate to formaldehyde, and this reacts with chromotropic acid solution to give a red colour which is measured colorimetrically.

Apparatus

1. Fractional distillation apparatus with variable reflux ratio capable of meeting the efficiency requirement detailed under **Method**. A column, 350 mm long, and 10 mm internal diameter, packed with 4-mm diameter, single turn, glass helices has proved satisfactory. The apparatus must be thermally insulated.
2. Pipettes (1-ml).
3. Pipette (2-ml) or a burette capable of delivering 2.0-ml aliquots.
4. Volumetric flasks (50-ml).
5. Volumetric flasks (3-ml) or 5-ml or 10-ml measuring cylinders.
6. Measuring cylinder (15-ml) or other measure to transfer 15 ± 0.5 ml of concentrated sulphuric acid.
7. Water baths maintained at 68°C and 20°C; ice bath.
8. Spectrophotometer capable of operation at 575 nm, or an absorptiometer fitted with a filter centred as close to 575 nm as possible.
9. Cells of 10-mm path length for spectrophotometer.

Reagents

1. *Sodium-1,8-dihydroxynaphthalene-3,6-disulphonate solution (chromotropic acid sodium salt soln.):* A 5 per cent. w/v solution in water, filtered if not clear. The solution should not be kept for more than a week.
2. *Sodium bisulphite or sodium metabisulphite crystals.*

3. *Sulphuric acid (concentrated; A.R. grade).*
4. *Oxidising solution:* A solution containing 3 g of potassium permanganate and 15 ml of orthophosphoric acid in 100 ml of water. Prepare monthly.
5. *Standard methanol soln. (0.01 per cent., w/v):* A solution containing 0.01 g of methanol (A.R.) made up to 100 ml with a 5.5 per cent. v/v solution of ethanol in water.
6. *Aqueous alcohol:* A 5.5 per cent. v/v solution of ethanol in water.

Method

Place 50.0 ml of sample (adjusted to contain 40 per cent. of spirit), in the fractional distillation apparatus and boil under total reflux for 3 hours in order to stabilise the fractionating column. Draw off two 3.0 ml fractions each over a period of 10 minutes. Dilute each fraction to 50 ml with water to give solutions containing approximately 5.5 per cent. of ethanol (v/v). To each of four 50-ml volumetric flasks A, B, C and D add 2.0 ml of oxidising solution, and chill the flasks in the ice bath (Note 1). Add to flask A, 1.0 ml of the first diluted fraction, to flask B 1.0 ml of the second diluted fraction, to flask C 1.0 ml of methanol solution and to flask D 1.0 ml of 5.5 per cent. (v/v) aqueous ethanol solution. Stopper the flasks and retain them in the ice bath for 30 minutes.

Decolorise the solutions by adding a few crystals of sodium bisulphite or metabisulphite and then add 1.0 ml of chromotropic acid solution. Add 15 ± 0.5 ml of concentrated sulphuric acid to each flask in turn while swirling the contents. Heat the flasks at 68°C for 15 minutes and then cool them in ice. Make up the volumes to 50 ml at 20°C. Keep the flasks at 20°C for 1 hour (Notes 2 and 3). Measure the optical densities at 575 nm of the solutions in flasks A, B and C relative to that in D, using 10-mm cells.

The recovery factor, F , is the fraction of the total methanol present which distils in the first fraction. If A, B, C are the optical densities of the respective solutions in flasks A, B, C, the still is of satisfactory efficiency if B is not more than 0.2A. If the optical density of the first distillate fraction is undesirably high for the colorimeter used, further dilute the fractions R times with 5.5 per cent. (v/v) ethanol solution and repeat the determination.

Calculation

$$F = 1 - B/A$$

Concentration of methanol in sample

$$= 25 R A/CF \text{ g per 100 litres of ethanol}$$

Notes on Procedure

1. The accuracy of the colorimetric reaction mainly depends on the reproducibility of the technique used for each stage. Each of the solutions must be treated in a precisely similar manner.

2. The temperature of the solutions must not differ from 20°C by more than $\pm 0.5^\circ\text{C}$ during the colorimetric measurements as the depth of colour varies with the temperature.
3. The absorbances of the solutions must be measured within 2 hours of the addition of the sulphuric acid as after that time the colour begins to fade.

B. GAS CHROMATOGRAPHIC METHODS

Methods 1, 3 and 4 of the First Report¹ may be used for the estimation of methanol in spirits. Hence methanol can be estimated together with the higher alcohols in a spirit by following any of the three procedures. When methanol alone is to be estimated, a modified version of Method 3¹ is recommended as follows:

ESTIMATION OF METHANOL IN POTABLE SPIRITS

Principle Water, methanol, acetaldehyde and methyl formate are eluted in that order from a column with porous polymer beads stationary phase. All other components of potable spirits, and acetone, have longer retention times and do not interfere. The methyl formate is added as the internal standard.

Apparatus and Operating Conditions (as for Method 3)

The operating conditions found suitable for the gas chromatograph are: Isothermal in the range 70–125°C; flame ionisation detectors; 2–5 μl injections and approximately 15 ml per minute carrier gas flow (nitrogen is suitable). Column 1.5 m $\times$ 4 mm i.d.

Reagents

1. *Ethanol free from methanol*: Ethanol for preparation of standard methanol solutions can be freed from methanol, if necessary, by fractional distillation as described in Method A.
2. *Methyl formate soln.*: Weigh 0.5 g methyl formate and make up to 200 ml with acetone (A.R.). Methyl formate is not stable in 40 per cent. (v/v) ethanol solution and because of its low boiling point evaporates from an acetone solution. It must therefore be standardised at frequent intervals against standard solutions of methanol in 40 per cent. (v/v) ethanol.
3. *Standard Methanol Solutions*:
 - (a) Weigh accurately 1.00 g of methanol and make to 100 ml with 40 per cent. (v/v) aqueous ethanol solution.
 - (b) Dilute 25 ml of the methanol solution (a) to 100 ml with 40 per cent. (v/v) aqueous ethanol solution.
 - (c) Dilute 1.00, 3.00, 5.00 and 7.00 ml aliquots of the methanol solution (b) to 100 ml with 40 per cent. (v/v) aqueous ethanol solution. This gives four standard solutions containing respectively 2.5, 7.5, 12.5 and 17.5 grammes of methanol per 100 litres of solution (6.3, 18.8, 31.3, 43.8 grammes of methanol per 100 litres of ethanol).

TABLE I
RESULTS OF A COLLABORATIVE STUDY OF THE GLC AND COLORIMETRIC
METHODS FOR THE DETERMINATION OF METHANOL

Sample	Method	Analyst						Mean	Rel. St. Deviation per cent.
		1	2	3	4	5	6		
<i>grammes of methanol per 100 litres of ethanol.</i>									
1. Grain spirit	GLC	21 18	22 22(c)	23 22(a) 21(b)	25	26		22	10
	Colori- metric			20	23		18	20	10
2. Rum	GLC	8.2 7.7	5.7 7.2(c)	10.0 8.8(a) 12.3(b)	7.4	9.0		8.5	21
	Colori- metric			13.6	8.3		6.2	9.4	33
3. Kirsch	GLC	450 440	490	390 570(b)	510	480		476	11
	Colori- metric			520	450		440	470	8
4. Grain Whisky	GLC	28 21	21 21(c)	22 20(a) 22(b)	20	25		22	11
	Colori- metric			21	20		22	21	3.9
5. Sample 4 + Metha- nol	GLC	31	36	33	38	35	34	35	6
	Colori- metric			35		34	39	36	6
6. Sample 4 + Metha- nol	GLC	39	40	39	43	40	39	40	3.5
	Colori- metric			43		42	46	44	3.9
7. Sample 4 + Metha- nol	GLC	43	47	44	52	44	45	46	7
	Colori- metric			45		45	48	46	3.1
8. Rum	GLC	6.1	5.0	7.5	5.6	5.0	4.3	5.6	18
	Colori- metric			4.7		7.5	3.8	5.3	30
9. Rum	GLC	3.1	3.4	4.8	2.9	3.3	2.3	3.3	23
	Colori- metric			4.9		7.0	1.9	4.6	45
10. Cane spirit A	GLC	4.3	4.3	6.3	5.7	4.3	3.0	4.6	23
	Colori- metric			6.6		4.5	3.0	4.7	31
11. Cane Spirit B	GLC	4.9	4.5	5.3	4.7	5.0	3.5	4.7	12
	Colori- metric			5.0		6.0	4.2	5.1	14
12. Malt Whisky	GLC	4.6	5.5	6.6	6.2	5.3	5.3	5.6	12
	Colori- metric			5.2		6.5	5.3	5.7	10

Notes. Column variations for GLC:

- (a) Stationary Phase—PEG 200 : Internal Standard—Butan-1-ol
 (b) Stationary Phase—Porous Polymer beads: Internal Standard—(none)
 (c) Stationary Phase—Porous Polymer beads: Internal Standard—Acetaldehyde
 Analyst (1) Stationary Phase—Porous Polymer beads: Internal Standard—Butan-1-ol
 Analyst (5) Stationary Phase—PEG 1500 : Internal Standard—Butan-1-ol
 Analyst (6) Stationary Phase—Porous Polymer beads: Internal Standard—Propan-2-ol

All other results were obtained with the conditions specified on page 51.

Method

Mix 10.0 ml of each of the four standard methanol solutions with 1.0 ml of the methyl formate internal standard solution. Use with the gas chromatograph according to the method described, connecting a recorder or integrator to measure the detector output. Adjust the sample to contain 40 per cent. (v/v) of ethanol. To 10.0 ml of this mixture add 1.00 ml of the internal standard solution and apply it to the chromatograph according to the method described.

Note: An apparatus with back-flushing facilities is desirable as examinations can then be completed in quick succession.

Calculation

Determine the peak height, area, or integrator response for the internal standard and for the methanol standards. Calculate the response factor R for methanol:—

$$R = ac/bd$$

where

a = concentration of methanol in mixture injected

b = response for methanol

c = response for internal standard

d = concentration of the internal standard in the mixture injected

R should be constant or nearly so for all the methanol standards.

If p = response of the internal standard when the concentration of the internal standard solution is 250 g per 100 litres of solution and q = response due to methanol with a response factor R , then:

Concentration of methanol in sample =

(250/10) (qR/p) grammes per 100 litres of solution at a strength of 40 per cent. (v/v) aqueous ethanol

= 62.5 (qR/p) grammes per 100 litres of ethanol.

COLLABORATIVE STUDY

Table I lists sets of results obtained from 12 samples submitted to collaborative study where both the various GLC and colorimetric methods were used. The GLC and colorimetric results are in good agreement with each other.

References

1. First Report of the Research Committee on the Analysis of Potable Spirits, *J. Assoc. Publ. Analysts*, 1970, **8**, 81.
2. Mathers, A. P., *J. Assoc. Offic. Agric. Chemists*, 1958, **41**, 121.
3. "Official Methods of Analysis of the Association of Official Analytical Chemists", Association of Official Analytical Chemists, 11th Edition, Washington D.C., 1970, p. 153.