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DETERMINATION OF ETHANOL IN BEER BY DIRECT INJECTION GAS CHROMATOGRAPHY: A COMPARISON OF SIX IDENTICAL SYSTEMS

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Six identical gas chromatographic (GC) systems from the same manufacturer were evaluated for the determination of ethanol in beers. Each system was assessed for detector linearity and drift using standard ethanol solutions. Repeatability (r_{95}) of each machine, repeatability (r_{95}) of the GC method and reproducibility (R_{95}) of the method over a range of ethanol concentrations (1–11% V/V) was determined using commercial beers. All six instruments were linear over the ethanol range 0–12% V/V and were in good agreement. Drift of the machines was negligible over the period of the analysis. Over the ethanol range 0.95 to 6.32% V/V the repeatability (r_{95}) and reproducibility (R_{95}) values were 0.050 and 0.083 respectively. Over the ethanol range 9.48 to 11.15% V/V the repeatability (r_{95}) and reproducibility (R_{95}) values were 0.153 and 0.227 respectively. Comparison of the precision values and those obtained in a recent IOB Analysis Committee Collaborative[1] for the determination of ethanol by gas chromatography showed no significant differences between the two methods. The reported method is suitable for determination of ethanol in beers.

Key Words: *Alcohol, beer (analysis method for), ethanol, gas chromatography*

INTRODUCTION

Ethanol determination by direct injection gas chromatography (GC) has been identified as suitable for the determination of ethanol in beers. The analysis is simple, rapid, easily automated and ideal for a large throughput of samples. Traceable, certified ethanol standards are available from the Laboratory of the Government Chemist (LGC). The advantages of GC over distillation[2] (IOB Method) are speed, automation and ethanol specificity. Nevertheless, distillation remains the reference method for ethanol determination.

Six identical GC systems (comprising of a Fisons 9000 GC, AS 800 auto-injector and DP 800 integrator) were purchased from Fisons Instruments, Crawley (UK) for the determination of ethanol in beers. This paper reports details of the precision data obtained for these systems.

EXPERIMENTAL

Sample Preparation

Beers were degassed by filtration through Whatman 2V filter papers. Samples for analysis were attemperated to 20°C and prepared by mixing 1.0 ml of sample or ethanol standard and 1.0 ml of 5% V/V iso-propanol as internal standard (British Drugs Houses, Poole, Dorset, UK. Analar grade) in a GC autosampler vial using an EDP electronic pipette (Anachem Ltd, Luton, Bedfordshire, UK). A 1 µl aliquot portion of the mixed contents was then injected onto the GC column using an auto-injector.

GC Conditions

Column:	Chromosorb 102, 80–100 mesh, 2 m × 2 mm i.d. (from Fisons)
Column oven:	170°C Isothermal
Injector:	225°C
Detector:	FID, 250°C
Run time:	4.5 minutes
Retention times:	Ethanol—1.75 minutes (approximately) iso-Propanol—2.75 minutes (approximately)
Carrier gas:	Nitrogen (200 kPa/17 ml min^{-1})

Analysis Performed

Standard ethanol solutions in the range 0–12% V/V were analysed on each GC system to determine detector linearity.

Twenty beer samples were selected for analysis over the approximate ethanol range 1–11% V/V and the following data was collected: Four samples with ethanol concentrations *ca.* 1, 3, 5 and 11% V/V were each prepared once and injected ten times on all six systems to determine the r_{95} of each GC; Five samples with ethanol concentrations *ca.* 1, 3, 5, 6 and 11% V/V were each prepared ten times and injected once on the GC systems to determine the r_{95} of the method; The twenty beer samples were each prepared once by six different analysts and analysed on the six GCs to determine the R_{95} of the method; An LGC 5% V/V ethanol sample was analysed every three hours over a period of forty-eight hours on each of the six systems to determine drift.

All samples were calibrated against an LGC nominal 5% V/V ethanol standard accredited to 5.05% V/V.

Each of the twenty beers was also analysed by distillation, according to the IOB Recommended Methods of Analysis[2], as a comparison.

RESULTS AND DISCUSSION

The r^2 values (Table I) from regression data for the standard ethanol calibration of the six systems shows all have a linear response up to at least 12% V/V ethanol. Gradients of each of the curves show all six systems to be in good agreement. Figure 1 is an example of the calibration graph obtained.

Repeatability (r_{95}) of the instruments (Table II) and the method (Table III) show that the r_{95} values increase as the ethanol concentration increases. These results suggest that two levels of precision data are required to cover the alcohol

TABLE I. Regression Data for Standard Ethanol Calibration Curves

Regression Data	GC					
	System 1	System 2	System 3	System 4	System 5	System 6
r^2	0.999	0.999	0.999	0.999	0.999	0.999
Gradient	0.184	0.183	0.182	0.182	0.179	0.182

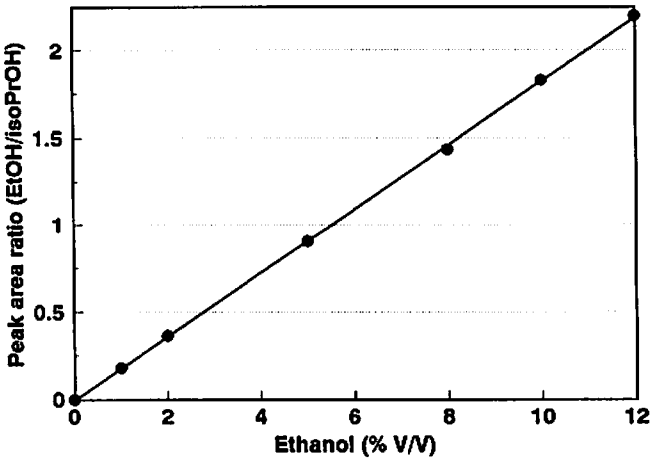

FIG. 1. Ethanol calibration graph. Average of triplicate analysis at each level.

TABLE II. Instrument r_{95} data

	GC					
Sample	System 1	System 2	System 3	System 4	System 5	System 6
Beer 2 1.06% V/V	0.013	0.012	0.012	0.009	0.020	0.012
Beer 5 3.56% V/V	0.026	0.035	0.035	0.014	0.020	0.030
Beer 14 5.21% V/V	0.037	0.045	0.042	0.045	0.044	0.049
Beer 20 11.15% V/V	0.110	0.093	0.099	0.046	0.089	0.061

TABLE III. Method r_{95} Data

	Beer Sample				
	Beer 2 1.06% V/V	Beer 5 3.57% V/V	Beer 14 5.24% V/V	Beer 18 6.33% V/V	Beer 20 11.11% V/V
Individual r_{95}	0.019	0.043	0.059	0.077	0.153

TABLE IV. Assessment of Instrument Drift over 48 hours

Analysis of 5.05% V/V LGC Standard at T=(h)	% V/V
T=0	5.06
T=3	5.09
T=6	5.07
T=9	5.05
T=12	5.05
T=15	5.07
T=18	5.07
T=21	5.05
T=24	5.04
T=27	5.06
T=30	5.05
T=33	5.07
T=36	5.07
T=39	5.06
T=42	5.06
T=45	5.05
T=48	5.04

TABLE V. R_{95} Data for individual beers analysed by GC and ethanol by Distillation Results

Sample	Ethanol by GC (% V/V) Average of 6 Systems	Ethanol by Distillation[2] (% V/V)— Average of 4	R_{95} for Individual Beers by GC
Beer 1	0.95	0.91	0.128
Beer 2	1.06	1.03	0.043
Beer 3	3.04	3.01	0.059
Beer 4	3.51	3.40	0.058
Beer 5	3.56	3.46	0.060
Beer 6	3.54	3.45	0.053
Beer 7	3.78	3.70	0.068
Beer 8	3.40	3.30	0.103
Beer 9	3.75	3.72	0.047
Beer 10	4.05	3.98	0.088
Beer 11	4.58	4.57	0.081
Beer 12	5.02	5.01	0.107
Beer 13	4.51	4.47	0.157
Beer 14	5.21	5.19	0.075
Beer 15	5.41	5.34	0.061
Beer 16	5.23	5.14	0.124
Beer 17	6.01	5.95	0.071
Beer 18	6.32	6.33	0.104
Beer 19	9.48	9.25	0.256
Beer 20	11.15	11.04	0.197

TABLE VI. Method Repeatability and Reproducibility Values

	Whitbread GC Method		IOB Collaborative GC Method[a]		IOB Distillation Method[b]
	Analysis Level (% V/V)		Analysis Level (% V/V)		Analysis Level (% V/V)
	1.06–6.36	9.48–11.15	0.93–6.02	9.17 (avg.)	2.64–4.56
r_{95}	0.050	0.153	0.061	0.154	0.076
R_{95}	0.083	0.227	0.136	0.284	0.182

[a]From: IOB Analysis Committee Collaborative Results[1].
[b]r_{95} and R_{95} data not available for alcohol levels greater than 4.56% V/V.

ranges of beers encountered. The data produced during this study suggested ranges of 1–7% V/V and 7–12% V/V (see Table VI).

Instrument drift and hence calibration drift was found to be less than the r_{95} of the method and therefore deemed negligible when assessed continuously over a 48-hour period (Table IV).

Average ethanol results from the six GC systems (Table V) are in good agreement with the distillation results, although, in all cases the GC ethanol figure was slightly higher than the corresponding distillation result by an average of 0.04% V/V. Unlike the repeatability (r_{95}) data, the reproducibility (R_{95}) data for the GC method indicates no relationship between ethanol concentration and R_{95} values, however, as with the repeatability values, two ranges are apparent: 1–7% V/V and 7–12% V/V.

Comparing the r_{95} and R_{95} data (Table VI) at the two identified ethanol levels, the GC method has marginally better precision than those reported by the IOB Analysis Committee for their GC method[1], although these differences are not significant. However, the procedures for obtaining the raw data for the two methods are different. The IOB recommended method for distillation has an R_{95} of 0.182 over the alcohol range 2–4.5% V/V and in comparison, the GC method has improved reproducibility over the same ethanol range (no precision data for higher ethanol content beers

is quoted in the IOB Recommended Methods of Analysis Manual).

Accuracy

The accuracy of the GC method was compared to that of the reference distillation method. For the purpose of this study the standard error of prediction 95% confidence limits (SEP_{95}) was employed (derived from the standard error of prediction—SEP[3]). The SEP_{95} for the GC method versus distillation is 0.121. It is generally thought that for a new method to be acceptable, the SEP_{95} must be less than the R_{95} of the reference method and ideally less than $R_{95}/(2)^{1/2}$. The calculated SEP_{95} is less than the R_{95} for distillation and is also marginally less than $R_{95}/(2)^{1/2}$ which is 0.129. The GC method is an acceptable alternative to the distillation method.

Conclusions

The six GC systems studied are in good agreement with each other and suitable for the measurement of ethanol in beers with an ethanol content of up to 12% V/V without the need for sample dilution prior to the addition of the internal standard.

There is no significant difference between the precision data obtained for the reported GC method and that of the IOB Analysis Committee GC method. The results show an improvement on the repeatability/reproducibility compared to the IOB Recommended Distillation Method.

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