



## European Brewery Convention

### EBC PRESS REPORT

# Determination of Alcohol in Low Alcohol and Non Alcohol Beers by Gas Chromatography-FID, Near Infra Red Spectroscopy and Catalytic Combustion Methods

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on behalf of the Analysis Committee of the European Brewery Convention

Methods for the determination of alcohol in low and non alcohol beers by gas chromatography with flame ionisation detection (GC-FID), near infra red spectroscopy (NIR) and catalytic combustion (CC) were collaboratively tested by the Analysis Committee of the European Brewery Convention according to ISO Standard 5725 in order to determine their suitability for publication in *Analytica-EBC*. Accuracy, repeatability ( $r_{95}$ ) and reproducibility ( $R_{95}$ ) values are presented.

The GC-FID method was found to have better within and between laboratory precision than the other two methods for the determination of alcohol in the non alcohol (0.007–0.08% V/V) beers and comparable precision for the low alcohol (0.37–0.81% V/V) beers. Over the whole range 0.007 to 0.81% V/V of alcohol, repeatability ( $r_{95}$ ) was found to be dependent on the mean value and was 0.096 m % V/V whereas reproducibility ( $R_{95}$ ) was found to be independent of the mean value and was 0.090% V/V. The gas chromatographic method is recommended for inclusion in *Analytica-EBC* as the reference method for the determination of alcohol in non and low alcohol (<1.0% V/V) beer samples.

The NIR and CC methods have acceptable within and between laboratory precision figures for the determination of alcohol in the low alcohol beers.

For the NIR method, repeatability ( $r_{95}$ ) and reproducibility ( $R_{95}$ ) were found to be independent of the mean value and were 0.022% V/V and 0.103% V/V respectively over the range of alcohol tested (0.007–0.81% V/V). The method is recommended for inclusion in *Analytica-EBC* for the determination of alcohol in low alcohol beer samples (>0.37% V/V).

For the CC method, both repeatability ( $r_{95}$ ) and the reproducibility ( $R_{95}$ ) were found to be independent of the mean and were 0.016% V/V and 0.087% V/V respectively over the range of alcohol tested (0.007–0.81% V/V). The method is recommended for inclusion in *Analytica-EBC* for the determination of alcohol in low alcohol (>0.37% V/V) beer samples.

## INTRODUCTION

The EBC Analysis Committee decided to carry out inter-laboratory ring tests on low and non alcohol beers (<1.0% V/V alcohol) using GC-FID, NIR and catalytic combustion equipment. The collaborative trial was carried out in autumn 2003 using ten beer samples with five different alcohol levels.

Nine laboratories took part in the collaborative trial with GC-FID, 17 laboratories with NIR and 18 laboratories with Catalytic Combustion equipment.

## EXPERIMENTAL

The organization of the collaborative trial and the statistical treatment of the data were performed according to the procedure given in the International Standard ISO 5725-2.

Ten beer samples, two from each different alcohol level and same production batches, were sent to participants. The participants analysed and reported both alcohol and specific gravity. A questionnaire regarding the equipment and calibration procedure used in the laboratory was also completed by each participant.

The published EBC Gas chromatographic and Catalytic Combustion methods and the EBC draft of the Near Infrared Spectroscopic method were used for the trial.

## RESULTS AND DISCUSSION

The original data for the GC-FID method are given in Table I. Mandel's k and h statistics were used for testing the consistency of results. For the GC-FID method there were four Mandel's h statistical outliers and one k outlier, which were excluded from the calculations. The results

**Table I.** Results: Raw data of Alcohol % V/V using GC-FID.

Lab	Beer samples									
	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2
1	0.037**	0.041**	0.110	0.111	0.461*	0.447*	0.618**	0.657**	0.991***	0.908***
2	0.010	0.010	0.08	0.08	0.32	0.33	0.49	0.53	0.80	0.85
3	0.007	0.009	0.082	0.081	0.38+	0.35+	0.53	0.51	0.78	0.75
4	0.007	0.008	0.072	0.070	0.32	0.34	0.50	0.53	0.80	0.81
5	0.007	0.008	0.070	0.073	0.37	0.38	0.53	0.54	0.81	0.84
6	0.006	0.005	0.075	0.079	0.40	0.40	0.55	0.55	0.82	0.82
7	0.036++	0.013++	0.081	0.077	0.38	0.39	0.53	0.54	0.83	0.85
8	0.011	0.011	0.077	0.081	0.39	0.38	0.50	0.54	0.77	0.82
9	0	0	0**	0**	0.38	0.37	0.51	0.50	0.81	0.79

\* = Mandel's h statistic straggler  
 \*\* = Mandel's h statistic outlier  
 + = Mandel's k statistic straggler  
 ++ = Mandel's k statistic outlier

**Table II.** Precision data of Alcohol % V/V using GC-FID.

	Beer samples				
	A	B	C	D	E
n <sub>r</sub>	7	8	9	8	8
n <sub>R</sub>	7	8	9	8	8
s <sub>r</sub> <sup>2</sup>	0.00000	0.00000	0.00011	0.00030	0.00048
S <sub>L</sub> <sup>2</sup>	0.0000	0.0002	0.0014	0.0001	0.0003
s <sub>r</sub>	0.0007	0.0020	0.0105	0.0173	0.0219
s <sub>R</sub>	0.0036	0.0125	0.0389	0.0194	0.0280
m	0.007	0.081	0.377	0.524	0.809
r <sub>95</sub>	0.002	0.007	0.034	0.058	0.073
R <sub>95</sub>	0.013	0.042	0.127	0.065	0.094
CVS <sub>r</sub>	10.00	2.44	2.79	3.31	2.71
CVS <sub>R</sub>	51.38	15.44	10.31	3.71	3.47

for the calculation of precision data for GC-FID are summarized in Table II. There is a strong significant relationship between repeatability r<sub>95</sub> and the mean, but the reproducibility R<sub>95</sub> is not dependent on the mean. The final r<sub>95</sub> and R<sub>95</sub> values for GC-FID method are:

$$r_{95} = 0.096 \text{ m} \quad R_{95} = 0.090$$

The original data for the NIR method are given in Table III. For the NIR method there were three Mandel's h statistical outliers and also three k outliers, which were excluded from the calculations. The results for the calculation of precision data for NIR are summarized in Table IV. For the NIR method both repeatability, r<sub>95</sub>, and reproducibility, R<sub>95</sub>, have no tendency to increase with higher mean values. The final r<sub>95</sub> and R<sub>95</sub> values for NIR method are:

$$r_{95} = 0.022 \quad R_{95} = 0.103$$

Because 15 of the total 17 participants using NIR equipment were using equipment from Anton Paar, precision data was also calculated separately using only the data from the Anton Paar analysers. The results for the calculation of precision data for the NIR Anton Paar analysers only are shown in Table V.

Here also there was no significant relationship between repeatability, r<sub>95</sub>, or reproducibility, R<sub>95</sub>, and the mean. The final values are:

$$r_{95} = 0.022 \quad R_{95} = 0.073$$

**Table III.** Results: Raw data of Alcohol % V/V using NIR.

Lab	Beer samples									
	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2
1	0.00	0.00	0.07	0.07	0.36	0.37	0.52	0.52	0.82	0.81
2	0.00	-0.01	0.07	0.07	0.37	0.36	0.52	0.52	0.80	0.79
3	0.02	0.02	0.10++	0.15++	0.39	0.39	0.55	0.55	0.82	0.82
4	-0.02	-0.02	0.06	0.06	0.35	0.35	0.52	0.52	0.80	0.80
5	-0.02	-0.03	-0.06*	-0.04*	0.36	0.38	0.53	0.53	0.82	0.80
6	0.02	0.02	0.08	0.09	0.38	0.39	0.56	0.56	0.83	0.82
7	0.01	0.01	0.08	0.07	0.36	0.36	0.52	0.52	0.81	0.81
8	0.00	0.00	0.08	0.08	0.37	0.37	0.54	0.54	0.81	0.81
9	0.013+	0.026+	0.104	0.091	0.39	0.39	0.53	0.53	0.82	0.83
10	-0.03	-0.03	0.05	0.05	0.34	0.34	0.56+	0.50+	0.79	0.79
11	0.00	0.00	0.045	0.045	0.335	0.340	0.500	0.500	0.790	0.790
12	-0.02	-0.03	0.05	0.03	0.33***	0.26***	0.50++	0.58++	0.80	0.79
13	0.00	0.00	0.05	0.04	0.34	0.34	0.50	0.51	0.78	0.80
14	0.00	0.00	0.02	0.01	0.31	0.31	0.48	0.47	0.77	0.76
15	0.07	0.08	0.13	0.14	0.41	0.41	0.63	0.60	0.91*	0.89*
16	0.125**	0.125**	0.175*	0.175*	0.44*	0.44*	0.65**	0.65**	0.93**	0.93**
17	nr	nr	nr	0.08	nr	0.38	nr	0.54	nr	0.82

nr = no result  
 \* = Mandel's h statistic straggler  
 \*\* = Mandel's h statistic outlier  
 + = Mandel's k statistic straggler  
 ++ = Mandel's k statistic outlier

**Table IV.** Precision data of Alcohol % V/V using NIR.

	Beer samples				
	A	B	C	D	E
$n_r$	15	15	15	14	15
$n_R$	15	16	16	15	16
$s_r^2$	0.00002	0.00005	0.00002	0.00017	0.00006
$S_L^2$	0.0007	0.0025	0.0010	0.0009	0.0008
$s_r$	0.0044	0.0070	0.0049	0.0130	0.0077
$s_R$	0.0261	0.0502	0.0318	0.0330	0.0298
$m$	0.003	0.067	0.369	0.530	0.810
$r_{95}$	0.013	0.021	0.015	0.040	0.023
$R_{95}$	0.079	0.151	0.096	0.100	0.090
$CVS_r$	165.38	10.44	1.33	2.44	0.96
$CVS_R$	989.69	74.92	8.63	6.22	3.68

**Table V.** Precision data of Alcohol % V/V using NIR Anton Paar Analysers only.

	Beer samples				
	A	B	C	D	E
$n_r$	14	13	13	13	14
$n_R$	14	14	14	14	15
$s_r^2$	0.00002	0.00005	0.00003	0.00015	0.00005
$S_L^2$	0.0003	0.0014	0.0005	0.0004	0.0003
$s_r$	0.0041	0.0073	0.0053	0.0121	0.0071
$s_R$	0.0173	0.0378	0.0236	0.0232	0.0174
$m$	-0.003	0.054	0.361	0.524	0.804
$r_{95}$	0.013	0.022	0.016	0.037	0.022
$R_{95}$	0.053	0.115	0.072	0.071	0.053
$CVS_r$	-161.40	13.32	1.46	2.31	0.88
$CVS_R$	-680.79	69.37	6.53	4.43	2.17

**Table VI.** Results: Raw data of Alcohol % V/V using Catalytic Combustion.

Lab	Beer samples									
	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2
1	0.012	0.009	0.081	0.078	0.41	0.41	0.56	0.56	0.86	0.86
2	0.02	0.01	0.08	0.09	0.37	0.38	0.50	0.50	0.79	0.79
3	-0.03**	-0.04**	0.03	0.02	0.32	0.32	0.45	0.45	0.73	0.74
4	0.02	0.01	0.07	0.06	0.36	0.36	0.51	0.50	0.82	0.81
5	0.01	0.00	0.06	0.06	0.36	0.36	0.50	0.50	0.82	0.82
6	0.001	0.000	0.045	0.042	0.30*	0.28*	0.41*	0.40*	0.63**	0.63**
7	0.01	0.00	0.06	0.06	0.37	0.37	0.50	0.51	0.81	0.81
8	0.013	0.003	0.067	0.063	0.38	0.39	0.52	0.53	0.83	0.81
9	0.012	0.013	0.122*	0.125*	0.42	0.42	0.58	0.59	0.83	0.83
10	0.012	0.014	0.071	0.075	0.37	0.37	0.53	0.54	0.80	0.81
11	0.01	0.01	0.07	0.07	0.38	0.39	0.54	0.53	0.80	0.80
12	0.03++	0.01++	0.08	0.07	0.38	0.36	0.50	0.49	0.80	0.78
13	0.016	0.017	0.086	0.089	0.396	0.399	0.530	0.538	0.79	0.80
14	0.00	0.00	0.04	0.04	0.31	0.31	0.43	0.43	0.78	0.77
15	0.00	0.00	0.07	0.06	0.39++	0.36++	0.51	0.50	0.84++	0.81++
16	0.000	-0.004	0.038	0.030	0.33	0.33	0.47	0.47	0.76	0.76
17		-0.02		0.04		0.35		0.48		0.76
18		0.03		0.09		0.39		0.51		0.79

\* = Mandel's **h** statistic straggler\*\* = Mandel's **h** statistic outlier+ = Mandel's **k** statistic straggler++ = Mandel's **k** statistic outlier**Table VII.** Precision data of Alcohol % V/V using Catalytic Combustion.

	Beer samples				
	A	B	C	D	E
$n_r$	14	16	15	16	14
$n_R$	16	18	17	18	16
$s_r^2$	0.00002	0.00002	0.00004	0.00003	0.00005
$S_L^2$	0.0001	0.0006	0.0013	0.0020	0.0009
$s_r$	0.0044	0.0044	0.0061	0.0055	0.0068
$s_R$	0.0096	0.0239	0.0362	0.0453	0.0310
$m$	0.007	0.066	0.364	0.502	0.797
$r_{95}$	0.013	0.013	0.018	0.017	0.021
$R_{95}$	0.029	0.071	0.108	0.135	0.093
$CVS_r$	58.61	6.77	1.67	1.09	0.85
$CVS_R$	128.51	36.47	9.93	9.02	3.88

The original data for the catalytic combustion method are given in Table VI. For the catalytic combustion method there were two Mandel's **h** statistical outliers and three **k** outliers, which were excluded from the computation. The results for the calculation of precision data for Catalytic Combustion are summarized in Table VII. Both repeat-

ability ( $r_{95}$ ) and reproducibility ( $R_{95}$ ) are not dependent on the mean. The final values are:

$$r_{95} = 0.016 \quad R_{95} = 0.087$$

The number of participating laboratories, the mean values and the  $r_{95}$  and  $R_{95}$  values are summarized at different sample levels for GC-FID, NIR and CC methods in Table VIII.

## CONCLUSIONS

The Gas Chromatographic-FID method for the determination of alcohol in low alcohol and non alcohol beers yields results with acceptable repeatability ( $r_{95}$ ) and reproducibility ( $R_{95}$ ). The EBC Analysis Committee recommend the GC-FID method as a reference method for determination of alcohol in low and non alcohol beer samples (<1.0% V/V).

The NIR method for determination of alcohol in low alcohol beers yields results with acceptable repeatability

**Table VIII.** Results: Alcohol % V/V summary table for different sample levels.

	GC-FID	NIR	NIR, AP only	CC
Level A				
labs	7/7	15/15	14/14	14/16
m	0.007	0.003	-0.003	0.007
r <sub>95</sub>	0.002	0.013	0.013	0.013
R <sub>95</sub>	0.013	0.079	0.053	0.029
Level B				
labs	8/8	15/16	13/ 14	16/18
m	0.081	0.067	0.054	0.066
r <sub>95</sub>	0.007	0.021	0.022	0.013
R <sub>95</sub>	0.042	0.151	0.115	0.071
Level C				
labs	9/9	15/16	13/14	15/17
m	0.38	0.37	0.36	0.36
r <sub>95</sub>	0.034	0.015	0.016	0.018
R <sub>95</sub>	0.127	0.096	0.072	0.108
Level D				
labs	8/8	14/15	13/14	16/18
m	0.52	0.53	0.52	0.50
r <sub>95</sub>	0.058	0.040	0.037	0.017
R <sub>95</sub>	0.065	0.100	0.071	0.135
Level E				
labs	8/8	15/16	14/15	14/16
m	0.81	0.81	0.80	0.80
r <sub>95</sub>	0.073	0.023	0.022	0.021
R <sub>95</sub>	0.094	0.090	0.053	0.093

(r<sub>95</sub>) and reproducibility (R<sub>95</sub>). The EBC Analysis Committee decided to include the method in Analytica-EBC and to recommend the NIR method for determination of alcohol in low alcohol beer samples (>0.37% V/V).

The Catalytic Combustion method for determination of alcohol in low alcohol beers yields results with acceptable repeatability (r<sub>95</sub>) and reproducibility (R<sub>95</sub>). The EBC Analysis Committee decided to recommend the Catalytic Combustion method for determination of alcohol in low alcohol beer samples (>0.37% V/V).

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