European Brewery Convention

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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Methods for the determination of alcohol in low and non alcohol beers by gas chromatography with flame ionization 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 analyzed 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 1. 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 for the calculation of precision data for GC-FID are summarized in table 2. There is a strong significant relationship between repeatability r_{95} and the mean, but the reproducibility R_{95} is not dependent on the mean. The final r_{95} and R_{95} values for GC-FID method are:

r_{95} = 0,096 m $\qquad$ R_{95} = 0,090

The original data for the NIR method are given in table 3. 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 4. For the NIR method both repeatability, r_{95}, and reproducibility, R_{95}, have no tendency to increase with higher mean values. The final r_{95} and R_{95} values for NIR method are:

r_{95} = 0,022 $\qquad$ 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 analyzers. The results for the calculation of precision data for the NIR Anton Paar analyzers only are shown in table 5.
Here also there was no significant relationship between repeatability, r_{95}, or reproducibility, R_{95}, and the mean. The final values are:

r_{95} = 0,022 $\qquad$ R_{95} = 0,073

The original data for the catalytic combustion method are given in table 6. 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 7. Both repeatability (r_{95}) and reproducibility (R_{95}) are not dependent on the mean. The final values are:

r_{95} = 0,016 $\qquad$ 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 8.

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 (r_{95}) and reproducibility (R_{95}). 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_{95}) and reproducibility (R_{95}). The EBC Analysis Committee decided to recommend the Catalytic Combustion method for determination of alcohol in low alcohol beer samples (>0,37 % V/V).

Bibliography

1. Analytica-EBC, 1998, Section 9 Beer, Method 9.2.4. Ethanol in Beer by Gas Chromatography.
2. Institute of Brewing Methods of Analysis, 1997, Section 9 Beer, Method 9.9.2, Alcohol in Beer: Near Infrared Spectroscopic Method.
3. Analytica-EBC, 1998, Section 9 Beer, Method 9.2.2, Alcohol in Beer by Catalytic Combustion.
4. International Standard ISO 5725:1994.

Table 1: Results: Raw data of Alcohol % V/V using GC-FID.

	Beer samples									
Lab	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 2: Precision data of Alcohol % V/V using GC-FID.

	Beer samples				
	A	B	C	D	E
n_r	7	8	9	8	8
n_R	7	8	9	8	8
s_r^2	0,00000	0,00000	0,00011	0,00030	0,00048
S_L^2	0,0000	0,0002	0,0014	0,0001	0,0003
s_r	0,0007	0,0020	0,0105	0,0173	0,0219
s_R	0,0036	0,0125	0,0389	0,0194	0,0280
m	0,007	0,081	0,377	0,524	0,809
r_{95}	0,002	0,007	0,034	0,058	0,073
R_{95}	0,013	0,042	0,127	0,065	0,094
CVS_r	10,00	2,44	2,79	3,31	2,71
CVS_R	51,38	15,44	10,31	3,71	3,47

Table 3: Results: Raw data of Alcohol % V/V using NIR.

	Beer Samples									
Lab	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 4: 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 5: Precision data of Alcohol % V/V using NIR Anton Paar Analyzers 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 6: Results: Raw data of Alcohol % V/V using Catalytic Combustion.

	Beer samples									
Lab	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 7: 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

Table 8: 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_{95}	0,002	0,013	0,013	0,013
R_{95}	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_{95}	0,007	0,021	0,022	0,013
R_{95}	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_{95}	0,034	0,015	0,016	0,018
R_{95}	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_{95}	0,058	0,040	0,037	0,017
R_{95}	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_{95}	0,073	0,023	0,022	0,021
R_{95}	0,094	0,090	0,053	0,093