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Determination of CO₂ in packaged beer by a manual pressure/temperature (P/T) method – determination of the repeatability and reproducibility

Submitted on behalf of the Analysis Committee of the European Brewery Convention

The determination of CO₂ in packaged beer by a manual pressure/temperature (P/T) method was collaboratively tested by the Analysis Committee of the European Brewery Convention according to ISO Standard 5725 in order to determine its suitability for publication in *Analytica-EBC*. Repeatability (r_{95}) and reproducibility (R_{95}) values are presented.

Repeatability (r_{95}) was found to be independent on the mean value and was 0,12 g/l over the range 4,8 to 7,0 g/l. Reproducibility (R_{95}) was found to be dependent on the mean and was 0,089m g/l over the range of CO₂ tested.

The method has acceptable repeatability and reproducibility and is recommended for inclusion in *Analytica-EBC*.

At the same time an instrumental thermal conductivity method using the Micro Logger 3654 analyzer from Hach Ultra Analytics was also collaboratively tested in order to determine its repeatability (r_{95}) and reproducibility (R_{95}) values.

Repeatability (r_{95}) was found to be independent on the mean value and was 0,08 g/l over the range 4,7 to 6,9 g/l. Reproducibility (R_{95}) was found to be dependent on the mean and was 0,054m g/l over the range of CO₂ tested.

The instrumental thermal conductivity using the Micro Logger 3654 analyzer from Hach Ultra Analytics is also recommended for inclusion in *Analytica-EBC*.

Descriptoren: *Analytica-EBC*, method development, determination of CO₂

1 Introduction

The Analysis Committee of the European Brewing Convention (EBC) decided to collaboratively test a manual pressure/temperature procedure for the determination of CO₂ in packaged beer.

23 laboratories participated in the test. Additional information was requested about the instrument used, the calculation formula or system and the corrections applied for the air in the head space.

At the same time a method for the determination of CO₂ using thermal conductivity based on one instrument from the company Hach Ultra Analytics, Switzerland (the Micro Logger 3654) was also tested to evaluate its performance.

2 Experimental

The organization of the collaborative trial and the statistical treatment of the data were performed according to the International Standard ISO 5725-21.

In the trial the method was tested with three beers having a range of CO₂ values between 4,8 and 7,0 g/l. Two bottles of each beer sample were sent in duplicate to each laboratory.

3 Results and discussion

Original data from the collaborative trial (but recalculated from original P/T values in the manual determination using the same Haffmans formula in order to homogenize the way the P & T are

converted into CO₂ concentration of the beer) is given in Tables 1, 2 and 3. For the manual P/T method four outliers were detected and excluded from the calculations. For the instrumental thermal conductivity method two outliers were detected and also excluded from the calculation.

Precision data are summarized in table 4, 5 and 6. Repeatability and reproducibility were calculated excluding the outliers and were considered satisfactory for both the manual and the instrumental methods.

4 Conclusion

Repeatability and reproducibility results for the determination of the CO₂ in packaged beer by a manual P/T method or by an instrumental method based on thermal conductivity using a Micro Logger 3654 from Hach Ultra Analytics (Switzerland) are acceptable. The EBC Analysis Committee has recommended the inclusion of both methods in *Analytica-EBC*.

5 Bibliography

1. International Standard ISO 5725-2, 1994.

Appendix

Table 1 Manual P/T Method

Raw data recalculated with the same Haffmans formula (g/l)

Lab.	A1	A2	B1	B2	C1	C2	Apparatus System	Calculation Space released	Air Head beers	S.G.
1	5,39	5,43	4,81*	4,92*	7,06	7,08	?	Wallerstein Rule	Not	1,01080 1,00709 1,00705
2	5,18	5,33	4,75	4,84	6,58	6,65	Zahm&Nagel Modified Piercing device	ASBC table	Not	1,01087 1,00702 1,01071
3	5,57	5,57	5,01**	4,85**	7,37	7,37	Zahm&Nagel D.T Piercing Device	Haffmans formula	Yes	? ? ?
4	5,52	5,58	5,02	5,06	7,30	7,23	Haffmans Inpack 2000	Haffmans formula	Yes	1,01083 1,00704 1,01063
5	5,23	5,30	4,71	4,71	7,08	7,08	?	ASBC table	Not	? ? ?
6	5,22	5,26	4,73	4,77	6,85*	6,75*	Zahm&Nagel Series 11000	Haffmans formula	Yes	1,01083 1,00704 1,01063
7	5,42	5,34	4,94	4,97	6,92	6,85	Haffmans Inpack 2000	Haffmans formula	Yes	1,01083 1,00704 1,01063
8	5,82 ^{oo}	6,15 ^{oo}	5,33 ^{oo}	5,33 ^{oo}	4,76 ^{oo}	4,76 ^{oo}	VLSF 100.07.037800	Haffmans formula	Not	? ? ?
9	4,95 ^o	5,11 ^o	4,52 ^o	4,54 ^o	6,33	6,37	Terris/WQS	Haffmans Rule	Yes	1,01083 1,00704 1,01063
10	5,59	5,59	4,97	4,95	7,13	7,14	Steinfurth 91.7.3V	Haffmans formula	Not	1,01083 1,00704 1,01063
11	5,31	5,30	4,82	4,81	7,02	7,04	Haffmans Inpack 2000	Haffmans formula	Not	1,01083 1,00704 1,01063
12	5,72	5,79	4,98	5,02	7,34	7,29	Haffmans CBL	Haffmans formula	Not	1,01055 1,00682 1,01047
13	5,50	5,42	4,99	4,95	7,23	7,17	?	Slide Rule	Not	1,01088 1,00709 1,01063
14	5,35	5,35	4,84	4,81	6,91	6,91	Haffmans Inpack 2000	Haffmans formula	Not	1,01083 1,00704 1,01063
15	5,41	5,39	4,92	4,92	7,04	7,04	Haffmans Halu	Slide Rule	Not	1,01085 1,00711 1,01074

Table 1 Manual P/T Method (continued)

Lab.	A1	A2	B1	B2	C1	C2	Apparatus System	Calculation Space released	Air Head beers	S.G.
16	5,35	5,35	4,73	4,81	6,91	6,98	Piercing device+digital pressure meter	Haffmans formula	Yes	? ? ?
17	5,26**	5,60**	5,04	5,02	7,20	7,19	Haffmans Inpack 2000	Haffmans formula	Not	? ? ?
18	5,48	5,43	4,89	4,94	7,06	7,04	Steinfurth	Haffmans Rule	Not	1,01083 1,00704 1,01063
19	5,49	5,45	4,93	4,92	7,14	7,05	Haffmans ICM-045	Haffmans Formula	Not	1,01083 1,00704 1,01063
20	5,28	5,38	4,86	4,84	6,75	leaking sample	Stadler-Zeller	Haffmans Formula	Not	1,0108 1,0072 1,0108
21	5,33	5,29	4,79	4,77	6,94	6,98	Haffmans Inpack CO2 meter	Haffmans Formula	Not	1,01083 1,00704 1,01063
22	5,33	5,34	4,76	4,79	7,01	6,94	Haffmans Inpack CO2 meter	Haffmans Formula	Not	1,01083 1,00704 1,01063
23	5,39	5,38	4,79	4,79	7,05	7,05	Haffmans Inpack CO2 meter	Haffmans Formula	Not	1,01083 1,00704 1,01063
24	5,12	5,14	4,82	4,79	6,75	6,75	Haffmans Inpack 200	Slide Rule	Not	1,01083 1,00704 1,01063

** within laboratory outliers, rejected
 * within laboratory stragglers, retained
 °° between laboratory outliers, rejected
 ° between laboratory stragglers, retained

Table 2 Raw data (g/kg) Micro Logger 3654

Lab.	A1	A2	B1	B2	C1	C2
1	5,17	5,13	4,54°	4,57°	6,73	6,67
2	5,40°	5,47°	4,91**	4,79**	7,06	7,06
3	5,34	5,35	4,74	4,74	6,97*	6,88*
4	5,32	5,29	4,74	4,76	6,92	6,93
5	5,19	5,22	4,62	4,68	6,68	6,69
6	5,23**	5,11**	4,60	4,61	6,74	6,67
7	5,25	5,26	4,72	4,71	6,86	6,88
8	5,29	5,26	4,68	4,70	6,95	6,98
9	5,24	5,25	4,67	4,69	6,87	6,90
10	5,26	5,25	4,66	4,66	6,89	6,94

** within laboratory outliers, rejected
 * within laboratory stragglers, retained
 °° between laboratory outliers, rejected
 ° between laboratory stragglers, retained

Table 3 Raw data for the Haffmans instruments alone (g/l) recalculated with the same Haffmans formula

Lab.	A1	A2	B1	B2	C1	C2
1	5,52	5,58	5,02	5,06	7,30	7,23
2	5,42 *	5,34 *	4,94	4,97	6,92	6,85
3	5,31	5,30	4,82	4,81	7,02	7,04
4	5,72 °°	5,79 °°	4,98	5,02	7,34 °	7,29 °
5	5,35	5,35	4,84	4,81	6,91	6,91
6	5,41	5,39	4,92	4,92	7,04	7,04
7	5,35	5,35	4,73 **	4,81 **	6,91	6,98
8	5,49	5,45	4,93	4,92	7,14	7,05
9	5,33	5,29	4,79	4,77	6,94	6,98
10	5,33	5,34	4,76	4,79	7,01	6,94
11	5,39	5,38	4,79	4,79	7,05	7,05
12	5,12	5,14	4,82	4,79	6,75	6,75

** within laboratory outliers, rejected
 * within laboratory stragglers, retained
 °° between laboratory outlier, rejected
 ° between laboratory stragglers, retained

Table 4 CO₂ P/T calculated using the same Haffmans formula

	A	B	C
n	22	22	22
m	5,38	4,85	7,00
r ₉₅	0,14	0,11	0,10
R ₉₅	0,47	0,35	0,69
CVS _r	0,86	0,79	0,50
CVS _R	2,99	2,47	3,33

r₉₅ = 0,12
R₉₅ = 0,089m

Table 6 Haffmans instruments with CO₂ calculated using the same Haffmans formula

	A	B	C
n	11	11	12
m	5,36	4,88	7,02
r ₉₅	0,080	0,058	0,114
R ₉₅	0,335	0,303	0,493
CVS _r	0,48	0,38	0,52
CVS _R	1,99	1,97	2,26

r₉₅ = 0,08
R₉₅ = 0,066m

Table 5 Instrumental thermal conductivity – Hach Ultra Analytics

	A	B	C
n	9	9	10
m (gr/kg)	5,27	4,67	6,86
r ₉₅	0,075	0,059	0,105
R ₉₅	0,27	0,21	0,41
CVS _r	0,44	0,39	0,48
CVS _R	1,58	1,38	1,87
m (gr/l)	5,33	4,70	6,93

r₉₅ = 0,08
R₉₅ = 0,054m