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DETERMINATION OF TOTAL NITROGEN IN BARLEY AND MALT BY COMBUSTION METHOD—COLLABORATIVE TRIAL

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A combustion method, relying on the Dumas principle, for the determination of total nitrogen in barley and malt, has been collaboratively tested by the Analysis Committee of the European Brewery Convention. Repeatability, r_{95}, and reproducibility, R_{95}, values were 0.063 and 0.116% of dry matter, respectively, for samples with nitrogen contents in the range 1.23 to 1.86% N of dry matter. There was no significant difference between these values for barley and malt. The Analysis Committee approved the adoption of the combustion method for inclusion in Analytica EBC as an alternative method.

Key words: *Collaborative trial, barley (analysis method for), malt (analysis method for), total nitrogen (determination of)*

INTRODUCTION

With recent instrumental developments, combustion methods relying on the Dumas principle, have shown to be promising and to provide a practical alternative to the Kjeldahl method for the determination of total nitrogen in feeds, food products and raw materials. Advantages of the combustion method are speed of analysis and the omission of harsh and toxical chemicals. Several organisations working with standardisation and recommendation of chemical methods have approved combustion methods for the determination of nitrogen. Of those related to brewing, The American Society of Brewing Chemists (ASBC) has approved combustion methods for nitrogen determination in brewing grains[1] as well as in wort and beer[2]. The Institute of Brewing has a combustion method as the reference method for total nitrogen determination in barley and malt, but not yet for wort and beer[3].

A comparison of the combustion method with the Kjeldahl method has shown that the former gives slightly higher nitrogen values, due to a more complete conversion of nitrogenous constituents. This implies the necessity to specify which method to use in, for example contract situations.

The current recommended method of the European Brewery Convention (EBC) for determining the total nitrogen content of barley and malt relies on the Kjeldahl principle. In view of the growing use of the combustion method, the Analysis Committee of the EBC decided to test its precision, starting with the determination of nitrogen in barley and malt.

EXPERIMENTAL

The method tested is essentially the same as that accepted by the Institute of Brewing, but the instructions for sample amount have been changed and a performance check has been included.

The organisation of the collaborative trial and the statistical treatment of the data were carried out according to the International Standard ISO 5725[4]. A uniform level design was employed. Four samples of barley and four samples of malt were distributed, as whole kernels, to eighteen laboratories. The total nitrogen content (% of dry matter) ranged from 1.3 to 1.85 for the barley samples and from 1.23 to 1.86 for the malt samples. The laboratories that participated in the trial were brewery and malthouse laboratories as well as those from institutes and instrument manufacturers.

The participants were requested to report the results both on an "as is" basis and as a % of dry matter. Moisture was analysed according to the present EBC methods, i.e. at 130°C for barley and at 105°C for malt samples.

RESULT

The raw data for nitrogen in % of dry matter are presented in Table I for barley and in Table II for malt. Nineteen sets of results were obtained; one laboratory analysed the samples with two different types of instruments. One laboratory, number 15, reported only values as "% as is" for the barley samples, and one laboratory, number 7, performed only single determinations on sample A.

The testing for outlying data revealed that all of these were distributed among three laboratories. An instrumental problem in laboratory number 6, and standardisation problems in laboratory 7a, were identified. No explanation was given for laboratory number 14. As a consequence of this, all data from laboratories 6 and 7a were rejected before performing the calculations, while only outliers and stragglers were omitted from laboratory number 14. After this, the tests for outliers was applied again, but no further outlying data were identified.

The statistical results are summarised in Table III. Repeatability, r_{95}, ranged from 0.035 to 0.097% of dry matter and reproducibility, R_{95}, from 0.094 to 0.138% of dry matter. There was no significant difference between the precision data for barley and malt, respectively. With the exception of barley sample D, there was no difference between CV_R for the results given as "% as is" or in % of dry matter.

For the concentration range tested, 1.23 to 1.86% N of dry matter, the following mean values were obtained:

repeatability, r_{95}: 0.063% nitrogen of dry matter
reproducibility, R_{95}: 0.116% nitrogen of dry matter.

CONCLUSION

The Analysis Committee of EBC judged as acceptable both the repeatability and reproducibility values for determination of total nitrogen in barley and malt obtained by the combustion method, and the Committee has approved the inclusion in Analytica EBC. However, since the combustion method has not been tested and accepted, for the determination of nitrogen in wort and beer, it will be included as an alternative method to the Kjeldahl method.

REFERENCES

1. American Society of Brewing Chemists. *Report of Subcommittee on Total Nitrogen in Brewing Grains by Combustion Method.* J. Am. Soc. Brew. Chem. 1992, **50**, 147–148.
2. American Society of Brewing Chemists. *Report of Subcommittee on Total Nitrogen in Wort and Beer.* J. Am. Soc. Brew. Chem. 1993, **51**, 183–185.
3. Buckee, G. K. *Determination of total nitrogen in barley, malt and beer by Kjeldahl procedures and the Dumas combustion method—Collaborative trial.* J. Inst. Brew. 1994, **100**, 57–64.
4. International Standard, ISO 5725, *Precision of test methods, second edition*, 1986.

TABLE I Raw data for barley (% nitrogen of dry matter)

Laboratory	Sample A		Sample B		Sample C		Sample D	
1	1.864	1.841	1.543	1.552	1.787	1.752	1.300	1.322
2	1.921	1.906	1.563	1.561	1.799	1.830	1.314	1.340
3	1.823	1.844	1.512	1.517	1.766	1.765	1.316	1.303
4	1.891	1.865	1.531	1.515	1.774	1.774	1.308	1.306
5	1.765	1.767	1.451	1.458	1.669	1.653	1.271	1.261
6	1.651	1.559	1.202*††	1,385*††	1.521**	1.509**	1.110*	1.172*
7a	–	1.687	1.531	1.535	1.780	1.766	1.516††	1.259††
7b	–	1.694	1.512	1.501	1.745	1.727	1.255	1.224
8	1.925	1.872	1.551	1.570	1.851	1.796	1.297	1.297
9	1.834	1.826	1.511	1.511	1.743	1.745	1.298	1.304
10	1.852	1.896	1.539	1.534	1.792	1.816	1.309	1.297
11	1.823	1.858	1.527	1.546	1.793	1.785	1.368	1.387
12	1.858	1.851	1.573	1.551	1.806	1.817	1.354	1.340
13	1.848	1.782	1.499	1.484	1.725	1.734	1.291	1.251
14	1.752	1.754	1.405*	1.378*	1.380	1.735	1.363††	1.487††
15	–	–	–	–	–	–	–	–
16	1.862	1.923	1.544	1.473	1.844	1.819	1.333	1.284
17	1.862	1.892	1.466	1.511	1.721	1.749	1.255	1.286
18	1.854	1.879	1.495	1.513	1.769	1.707	1.267	1.269

*Cell average is a straggler according to Dixon's test ($p \leq 0.05$)
**Cell average is an outlier according to Dixon's test ($p \leq 0.01$)
†Cell difference is a straggler according to Cochran's test ($p \leq 0.05$)
††Cell difference is an outlier according to Cochran's test ($p \leq 0.01$)

TABLE II Raw data for malt (% nitrogen of dry matter)

Laboratory	Sample I		Sample J		Sample K		Sample L	
1	1.794	1.776	1.871	1.867	1.250	1.247	1.400	1.461
2	1.785	1.779	1.890	1.886	1.264	1.242	1.464	1.463
3	1.727	1.731	1.852	1.841	1.207	1.199	1.426	1.432
4	1.782	1.791	1.890	1.897	1.247	1.258	1.475	1.469
5	1.699	1.671	1.781	1.801	1.169	1.172	1.362	1.401
6	1.701	1.672	1.741	1.724	1.099	1.079	1.275	1.279
7a	1.960**	1.882**	2.004*	1.990*	1.373**	1.378**	1.497	1.555
7b	1.735	1.772	1.820	1.818	1.181	1.197	1.346	1.388
8	1.842	1.752	1.926	1.931	1.258	1.285	1.487	1.510
9	1.723	1.783	1.891	1.833	1.239	1.249	1.427	1.413
10	1.775	1.773	1.890	1.885	1.238	1.235	1.454	1.443
11	1.822	1.804	1.856	1.876	1.267	1.244	1.442	1.452
12	1.791	1.815	1.899	1.900	1.237	1.244	1.456	1.463
13	1.745	1.731	1.812	1.898	1.214	1.216	1.436	1.394
14	1.920††	1.625††	1.930	1.828	1.210††	1.112††	1.316	1.301
15	1.777	1.733	1.842	1.770	1.192	1.211	1.372	1.433
16	1.826	1.774	1.777	1.858	1.286	1.300	1.490	1.401
17	1.713	1.781	1.812	1.893	1.197	1.240	1.396	1.433
18	1.771	1.756	1.872	1.856	1.215	1.202	1.423	1.434

*Cell average is a straggler according to Dixon's test ($p \leq 0.05$)
**Cell average is an outlier according to Dixon's test ($p \leq 0.01$)
†Cell difference is a straggler according to Cochran's test ($p \leq 0.05$)
††Cell difference is an outlier according to Cochran's test ($p \leq 0.01$)

TABLE III Summary of statistical data (% N of dry matter)

Sample	m	s_r	r_{95}	S_R	R_{95}	Number of laboratories
Barley A	1.850	0.024	0.068	0.049	0.136	15
Barley B	1.520	0.018	0.050	0.033	0.093	15
Barley C	1.765	0.022	0.060	0.049	0.138	16
Barley D	1.300	0.016	0.046	0.037	0.102	15
Malt I	1.765	0.027	0.076	0.039	0.110	16
Malt J	1.860	0.035	0.097	0.044	0.122	17
Malt K	1.231	0.012	0.035	0.033	0.094	16
Malt L	1.425	0.026	0.073	0.048	0.134	17