

DETERMINATION OF REPEATABILITY AND REPRODUCIBILITY OF EBC ACCEPTED METHODS. III—BARLEY ANALYSIS

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Methods for barley analysis published in *Analytica EBC*, 4th ed. have been collaboratively tested by the European Brewery Convention Analysis Committee and other European laboratories involved in Barley analysis. Repeatability (r_{95}) and reproducibility (R_{95}) values are presented. The answers to a questionnaire sent to all participating laboratories are discussed.

Key Words: Collaborative test, Analysis method, Barley, precision.

INTRODUCTION

The same general procedure as for malt and laboratory wort described in a preceding paper¹ was followed. Definitions and an example can also be found in this paper.

Particular procedures associated with these tests are discussed under each paragraph.

Six barley samples, including a high-moisture sample, were sent to 32 laboratories. Duplicate results from 28 laboratories were obtained.

In some cases, the number of results was too low for a reliable evaluation of the precision. Values obtained in these cases are given in brackets.

RESULTS AND DISCUSSION

Complete results are given in Table I.

In this table, it can be seen that in some cases (germination and sieving tests), logarithmic equations relating r_{95} or R_{95} to the measured value m stick to actually obtained values better than linear equations. In those cases tables calculated from the equations in Table I are also given (Tables II to VIII).

The following example illustrates how to use these tables (Germinative capacity, EBC method 3.5.2).

- results of two single determinations in the same laboratory: 93.2% and 95.4%.
- mean value: 94.3%, rounded off to 94.5%.
- table 3 shows that for 94.5% the acceptable difference between results (r_{95}) is 3.0.

– the difference between the two values is: 2.2. It can be accepted.

– express the result as indicated in the method (in % as a whole number): 94.3% → 94%

Special comments are given for the following methods:

Moisture (EBC method 3.1)

Five samples, ranging from 11.5% to 13% and a high-moisture sample (21.5%) were used. Repeatability and reproducibility are judged to be related to the measured value, but as there is a large gap between 13% and 21.5%, the Analysis Committee decided to give separate values.

The same applies to ISO 712 method (determination of moisture in cereals at 130–133°C), which was accepted by the Analysis Committee to replace the present method (106°C).

Note: Method 3.1 was archived in May 1994 and replaced by method 3.1.1.—Moisture content (130–133°C).

Germination (EBC methods 3.5 and 3.6)

Precision values may differ from one method to another due to the number of grains analyzed. When using method 3.6.2 (BRF method) two sets of 100 grains should be analyzed in both 4 ml and 8 ml tests.

Too few results were obtained with method 3.6.3 (Schönfeld) and no statistics are published.

Sieving test (EBC method 3.8)

Results are only given for:

- the sum of fractions I and II (grains above 2.8 mm and 2.5 mm sieves) which is a commonly used value in trade
- fraction IV (grains under the 2.2 mm sieve, including damaged barley grains).

TABLE I. Repeatability and reproducibility of EBC barley analysis methods

Method		Range	Number of results	Repeatability r_{95}	Reproducibility R_{95}	See also
3.1 – Moisture (106°C)	%	11–13	27–28	$r = 0.16$	$R = 0.74$	
		21.5	28	$r = 0.39$	$R = 1.3$	
3.1.1 – Moisture (130–133°C)	%	11–13	14–15	$r = 0.13$	$R = 0.55$	
		21.7	14	$r = 0.27$	$R = 2.6$	
3.2 – Nitrogen	% dm	1.5–2.1	26–27	$r = 0.04$	$R = 0.10$	
3.3 – Thousand Corn Weight	g dm	33–40	19–23	$r = 1.1$	$R = 1.7$	
3.5 – Germinative Capacity	%					
3.5.1. – Staining method		70–100	12–13	$r = 2^* (100-m)^{0.25}$	$R = 95-0.9 m$	Table 2
3.5.2 – H ₂ O ₂ method		70–100	11–12	$r = 1.3^* (100-m)^{0.5}$	$R = 98-0.97 m$	Table 3
damaged grains		(0–2.5)	6	$(r = 0.1 + 0.4 m)$	$(R = 0.8 + 1.5 m)$	
3.6 – Germinative Energy	%					
3.6.1 – Aubry method 3 days		60–99	11	$r = 1.5^* (100-m)^{0.5}$	$R = 2^* (100-m)^{0.6}$	Table 4
Aubry method 5 days		70–99	10–11	$r = 1.4^* (100-m)^{0.5}$	$R = 1.9^* (100-m)^{0.7}$	Table 5
3.6.2 – BRF method, 4 ml		60–99	14–15	$r = 2.8^* (100-m)^{0.4}$	$R = 3^* (100-m)^{0.5}$	Table 6
BRF method, 8 ml		40–99	14–15	$r = 3^* (100-m)^{0.4}$	$R = 4^* (100-m)^{0.5}$	Table 7
3.8 – Sieving test	%					
(a) Fractions I + II		75–97	24–25	$r = 2.1$	$R = 20-0.18 m$	
(b) Fraction IV		0.3–3.8	19–25	$r = 0.6^* m^{0.6}$	$R = 1.1^* m^{0.6}$	Table 8
3.11.2 – Beta glucan (fluorometry)	% dm	3.6–4.3	8	$r = 0.3$	$R = 0.8$	

m = measured value

Values in brackets are only an indication (number of results too small)

TABLE II. Germinative capacity, EBC method 3.5.1 (Staining)

Germinative Capacity % (in half units)	Repeatability r_{95}	Reproducibility R_{95}
<85.0	>4.0	>19
85.0	4.0	19
85.5-86.0	4.0	18
86.5-87.0	4.0	17
87.5-88.0	4.0	16
88.5-89.0	3.5	15
89.5-90.5	3.5	14
91.0-91.5	3.5	13
92.0-92.5	3.5	12
93.0-93.5	3.0	11
94.0-95.0	3.0	10
95.5-96.0	3.0	9
96.5-97.0	2.5	8
97.5-98.0	2.5	7
98.5-99.0	2.0	6
>99	1.5	5

TABLE V. Germinative energy, EBC method 3.6.1 (Aubry, 5 days)

Germinative Energy % (rounded to the nearest half unit)	Repeatability r_{95}	Reproducibility R_{95}
<85	>5.5	>13
85.0-85.5	5.5	13
86.0-86.5	5.0	12
87.0-88.5	4.5	11
89.0-90.5	4.5	10
91.0-91.5	4.0	9
92.0-92.5	4.0	8
93.0-94.0	3.5	7
94.5-95.0	3.0	6
95.5-96.0	3.0	5
96.5-97.0	2.5	4
97.5-98.0	2.0	3
98.5-99.0	1.5	2
>99	1.0	2

TABLE III. Germinative capacity, EBC method 3.5.2 (H₂O₂)

Germinative Capacity % (rounded to the nearest half unit)	Repeatability r_{95}	Reproducibility R_{95}
<85.0	>5	>16
85.0	5.0	16
85.5-86.0	5.0	15
86.5-87.0	4.5	14
87.5-88.0	4.5	13
88.5-89.0	4.5	12
89.5-90.0	4.0	11
90.5-91.0	4.0	10
91.5-92.0	3.5	9
92.5-93.0	3.5	8
93.5-94.0	3.0	7
94.5-95.0	3.0	6
95.5-96.0	2.5	5
96.5-97.0	2.0	4
97.5-98.0	2.0	3
98.5-99.0	1.5	2
>99	1.0	2

TABLE VI. Germinative energy, EBC method 3.6.2 (BRF, 4 ml test)

Germinative Energy % (in half units)	Repeatability r_{95}	Reproducibility R_{95}
<85	>8	>12
85.0-87.0	8.0	11
87.5-89.0	7.5	10
89.5-90.5	7.0	9
91.0-91.5	6.5	9
92.0-92.5	6.5	8
93.0-93.5	6.0	8
94.0-95.0	5.5	7
95.5-96.0	5.0	6
96.5-97.0	4.5	5
97.5	4.0	5
98.0	3.5	4
98.5-99.0	3.0	3
>99	2.0	2

TABLE IV. Germinative energy, EBC method 3.6.1 (Aubry, 3 days)

Germinative Energy % (rounded to the nearest half unit)	Repeatability r_{95}	Reproducibility R_{95}
<85.0	>6.0	>10
85.0	6.0	10
85.5-86.5	5.5	10
87.0-87.5	5.5	9
88.0-88.5	5.0	9
89.0-89.5	5.0	8
90.0-90.5	4.5	8
91.0-91.5	4.5	7
92.0-92.5	4.0	7
93.0-93.5	4.0	6
94.0-94.5	3.5	6
95.0-96.0	3.0	5
96.5	3.0	4
97.0	2.5	4
97.5	2.5	3
98-98.5	2.0	3
99.0	1.5	2
>99	1.0	2

TABLE VII. Germinative energy, EBC method 3.6.2 (BRF, 8 ml test)

Germinative Energy % (in half units)	Repeatability r_{95}	Reproducibility R_{95}
<85	>8.5	>15
85.0-86.5	8.5	15
87.0-88.5	8.0	14
89.0-90.0	7.5	13
90.5-92.0	7.0	12
92.5-93.0	6.5	11
93.5-94.0	6.0	10
94.5-95.0	6.0	9
95.5-96.5	5.0	8
97.0-97.5	4.5	7
98.0	4.0	6
98.5	3.5	5
99.0	3.0	4
>99	2.0	3

TABLE VIII. Sieving test, EBC method 3.8, fraction IV

% under 2.2 mm, including damaged barley grains	Repeatability r_{95}	Reproducibility R_{95}
0.3	0.3	0.5
0.4-0.6	0.4	0.7
0.7-0.8	0.5	0.9
0.9-1.1	0.6	1.1
1.2-1.4	0.7	1.3
1.5-1.7	0.8	1.5
1.8-2.1	0.9	1.7
2.2-2.5	1.0	1.9
2.6-2.9	1.1	2.0
3.0-3.3	1.2	2.2
3.4-3.8	1.3	2.4

Precision values were better with Steinecker machines than with Sortimat machines, and systematic differences also appeared. For these reasons, only Steinecker machines as specified in the reference method should be used in trade or official analysis.

Beta Glucan

Too few results were obtained with method 3.11.1 (enzymic) and no statistics can be published.

BARLEY ANALYSIS QUESTIONNAIRE

A questionnaire was sent to all laboratories participating in the ring test in order to check materials, reagents and procedures actually used. From the answers received, the EBC Analysis Committee decided to publish the following comments and recommendations:

SAMPLING

Devices described in *Analytica EBC*, 4th ed. should be used systematically for:

- sample homogenization
- sampling before each determination.

When amounts of less than 30 g have to be taken for

analysis, special procedures must be followed, including division by means of a slot or rotating divider, followed by grain selection using a modified grain counter. This procedure was described in a booklet published in 1989².

MOISTURE

Ovens efficiency must be checked regularly.

NITROGEN

The exact Kjeldahl procedure is never used nowadays. Guidelines including recommendations about the determination of nitrogen according to the principles of Kjeldahl (ISO Standard no 1871) should be followed. In particular, blanks and efficiency tests (mineralisation and distillation) must be performed regularly.

GERMINATIVE CAPACITY

In method 3.5.1 all laboratories mentioned Triphenyl Tetrazolium Chloride as reagent.

GERMINATIVE ENERGY

In method 3.6.1 the exact material and procedure are used by very few laboratories. Metallic perforated plates, cotton wool and a measured quantity of water must be used systematically instead of glass plates and "wet" filter paper.

In method 3.6.2 (BRF) germinated grains must be removed daily.

SIEVING TEST

Grading machines must be checked regularly (slot width, timer, speed, length of travel, horizontality).

In old machines, an eccentric movement due to looseness may appear. This is a very critical point which must be repaired immediately, as it is the cause of serious errors.

REFERENCES

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