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Determination of the N-Nitrosodimethylamine Content of Beer and Malt (A Collaborative Trial)

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

After about fifteen years a study was carried out to determine the variation in results of the N-nitrosodimethylamine (NDMA) determination in beer and malt carried out in different laboratories, in order to obtain an overall view of the precision of the various methods used. Two collaborative trials were carried out by the EBC Analysis Committee during 1998. Repeatability values (r_{95}) for beer in the range of $0,09 \div 0,13$ and for malt $0,33 \div 0,42$ were found. Reproducibility values (R_{95}) for beer in the range of $0,45 \div 0,54$ and for malt $0,65 \div 4,08$ were obtained.

BC 34 Malt

(Descriptors: Collaborative trial, NDMA, N-nitrosodimethylamine, beer, malt.

Descriptoren: Ringanalyse, N-Nitrosodimethylamin, Bier, Malz).

1 Introduction

In April 1998 the first collaborative trial was carried out using three beer samples (two spiked with NDMA) and one commercial malt. Six participants took part in the trial on beer but only five returned malt results. Furthermore, after the statistical treatment the number of acceptable results was yet lower and so it was decided to repeat the collaborative trial with more participants. The second trial was carried out in October 1998.

2 Experimental

The organization of the collaborative trials and the statistical treatment of the data were carried out according to the procedures given in International Standards ISO 5725-1 and ISO 5725-2 (1, 2). A uniformly designed trial was employed and six samples were circulated to 11 participants: three beers (all spiked with NDMA; original beer $0,3 \mu\text{g/l}$ NDMA) and three commercial malts without NDMA additions. Laboratories were asked to determine the NDMA concentrations in duplicate to 1 decimal place. Beer results were obtained from six participants, malt results were submitted by 9 laboratories. Two laboratories did not send their results; one of them had been excused due to the TEA detector being out of order.

3 Results and discussion

The precision data from the first collaborative test are given in Table I for illustration only. Original data of the second collaborative trial are given in Table II. The participants used MEBAK methods (4, 5), ASBC methods (6), Drost method (3) or their own methods/modifications. For beer 1, beer 2 and malt A no outliers

Table I Summary of the precision data of the first trial (April 1998) [ppb]

Level	1	2	3	4
Sample	Beer 1	Beer 2	Beer 3	Malt
Number of laboratories	5	5	4	4
Grand mean	0.11	0.65	1.16	0.97
Repeatability standard deviation	0.003	0.021	0.036	0.035
Reproducibility standard deviation	0.013	0.052	0.111	0.085
Repeatability r_{95}	0.009	0.059	0.101	0.098
Reproducibility R_{95}	0.036	0.146	0.311	0.238

ppb... ($\mu\text{g/kg}$ or $\mu\text{g/l}$)
 Beer 1: no addition of NDMA; Beer 2: Beer 1 + $0,5 \mu\text{g/l}$ NDMA; Beer 3: Beer 1 + $1,0 \mu\text{g/l}$ NDMA

or stragglers were identified using Cochran's and Grubbs' test. Laboratory I for beer 3 was identified as a straggler using Grubbs' test. The same laboratory was identified as a straggler for malt B and an outlier for malt C using Cochran's test. The precision data are summarized in Table III. Values of r_{95} for the beer are in the range of $0,09 \div 0,13$ and for malt $0,33 \div 0,42$. Values of R_{95} for beer are in the range of $0,45 \div 0,54$ and for malt $0,65 \div 4,08$. Comparing these results with those obtained in 1982/1983 (3) we see that they are nearly identical. The situation in the field of the N-nitrosodimethylamine determination remains unchanged.

4 Conclusions

The Analysis Committee of the European Brewery Convention carried out two collaborative trials for the determination of the NDMA content in beers and malts. Participants used MEBAK methods, ASBC methods, the Drost method or in-house methods. The results of the trials indicate that the precision and accuracy of the methodology used is satisfactory. Therefore, there is no requirement to establish a harmonized methodology.

Table II Original data of the second collaborative trial (October 1998) [ppb]

Sample Lab	Beer 1		Beer 2		Beer 3		Malt A		Malt B		Malt C	
A	1.2	1.1	0.7	0.7	1.1	1.1	1.1	1.05	2.2	2.4	4.6	4.7
B	—	—	—	—	—	—	1.4	1.4	3.3	3.3	7.5	7.5
C	—	—	—	—	—	—	0.7	0.7	1.3	1.3	2.2	2.2
D	1.2	1.2	0.6	0.6	1.0	1.0	0.9	0.9	2.2	2.1	5.1	5.5
E	1.0	1.0	0.6	0.6	1.1	1.1	1.0	1.1	2.1	2.1	4.5	4.5
F	0.98	0.95	0.35	0.31	0.92	0.94	1.2	1.1	2.3	2.5	4.5	4.4
G	—	—	—	—	—	—	0.9	1.1	2.3	2.4	5.1	5.3
H	1.2	1.1	0.7	0.6	1.0	1.1	0.8	0.7	2.0	2.0	4.5	4.4
I	0.77	0.70	0.32	0.36	0.58*	0.61*	1.27	0.84	2.82 ⁺	2.27 ⁺	4.25 ⁺⁺	5.16 ⁺⁺
Mean ^o	1.06	1.01	0.55	0.53	0.95	0.97	1.03	0.99	2.28	2.26	4.69	4.85
Grand Mean	1.03		0.54		0.96		1.01		2.27		4.77	

ppb ... (µg/kg or µg/l)
⁺ Straggler at p = 0.05 based on Cochran's test ^{*} Straggler at p = 0.05 based on Grubbs' test ^o Mean excluding the outlier(s)
⁺⁺ Outlier at p = 0.01 based on Cochran's test ^{**} Outlier at p = 0.01 based on Grubbs' test
Spiking:
 Original beer: X = 0.3 µg/l ppb; Beer 1: X + 0.85 µg/l NDMA; Beer 2: X + 0.35 µg/l NDMA; Beer 3: X + 0.75 µg/l

Table III Summary of the precision data of the second trial (October 1998) [ppb]

Level	Sample	1 Beer 1	2 Beer 2	3 Beer 3	4 Malt A	5 Malt B	6 Malt C
Number of laboratories		6	6	6	9	9	8
Grand mean		1.03	0.54	0.96	1.00	2.27	4.77
Repeatability standard deviation		0.046	0.033	0.031	0.012	0.15	0.12
Reproducibility standard deviation		0.18	0.16	0.19	0.23	0.54	1.46
Repeatability r_{95}		0.13	0.09	0.09	0.34	0.42	0.33
Reproducibility R_{95}		0.49	0.45	0.54	0.65	1.50	4.08

ppb... (µg/kg or µg/l)

5 Zusammenfassung

Kellner, V.: Bestimmung des N-Nitrosodimethylamin-Gehaltes in Bier und Malz — Monatsschrift für Brauwissenschaft 52, Nr. 11/12, 207 – 208, 1999

BC3 Chemisch-technische Brauereibetriebskontrolle/34 Malz

Nach etwa 15 Jahren wurden voneinander abweichende Ergebnisse der Bestimmung des N-Nitrosodimethylamin (NDMA)-Gehaltes in Bier und Malz, wie sie in verschiedenen Laboratorien in diesem Zeitraum gewonnen wurden, untersucht, um einen Überblick über die Genauigkeit der verschiedenen angewandten Methoden zu gewinnen. Zwei Ringversuche wurden vom EBC Analysis Committee 1998 durchgeführt. Es wurden Wiederholungswerte (r_{95}) für Bier im Bereich 0,09 – 0,13 und für Malz 0,33 – 0,42 gefunden. Man erhielt reproduzierbare Werte (R_{95}) für Bier im Bereich von 0,45 – 0,54 und für Malz 0,65 – 4,08.

Kellner, V.: Détermination de la teneur en N-Nitrosodiméthylamine dans la bière et le malt — Monatsschrift für Brauwissenschaft 52, No 11/12, 207 – 208, 1999

BC3 Contrôle de fabrication en brasserie technique et chimique/34 malt

Après 15 années, on a trouvé des résultats aléatoires au niveau de la détermination de la N-Nitrosodiméthylamine (NDMA). Sa teneur dans la bière et le malt, trouvée par différents laboratoires au cours de ces quinze

années, a été évaluée et une synthèse a été faite sur la précision des différentes méthodes d'analyses appliquées. Deux tests interlaboratoires ont été effectués en 1998 par le Comité des Analyses de l'EBC. Les valeurs de répétabilité (r_{95}) dans la bière se situaient entre 0,09 et 0,13 et dans le malt entre 0,33 et 0,43. Les valeurs de reproductibilité (R_{95}) étaient dans la bière entre 0,45 et 0,54 et dans le malt entre 0,65 et 4,08.

6 References

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