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Furfural equivalent (FE) determination in brewing

Continuous flow analyser equipped with distillation unit, quartz flow cell and 275 nm UV detector was used for furfural equivalent (FE) value determination. The FE value comprises both furfural and other volatiles absorbances expressed in furfural concentration (µg.l^{-1}). The FE value is connected to sugar degradation, Maillard reaction and sensory active compound formation during food and beverage storage. The FE value can also be used as an indicator of brewing process consistency and for beverage ageing checking-up.

BC 35 Wort (hot wort)

(Descriptors: Furfural, beer ageing, shelf-life, sugar degradation, thermal damage.

Deskriptoren: Furfural, Bieralterung, chem.-phys. Stabilität, Zuckerabbau, Wärmeschädigung).

1 Introduction

Furfural and hydroxymethyl furfural (HMF) are often used as analytical indicators of beer and food deterioration (1, 2, 9). Both compounds can be formed simultaneously as a result of various reactions associated with sugar degradation. Their content in food is determined by both classical and modern analytical methods (5).

Spectrophotometric methods are usually based on the reaction between furfural and aniline in acidic solution or on those between HMF, barbituric acid and p-toluidine (3, 12). Furfural as a volatile matter is usually isolated by steam distillation while HMF is a non volatile compound. Aniline number determination uses the same principle (11).

The furfural content can be directly determined by absorbance measurement of the steam distillate at 277 nm (6). *Klein* et al. used absorption integral (AI) connected to absorption curve area between 240 and 310 nm using spectrophotometry of steam-distilled beer (4). The distillate contained furfural, absorbing at 277 nm besides other compounds.

Furfural and HMF are usually expected to be produced from pentoses and hexoses during their acid hydrolysis. Their formation has also been considered as a result of radical sugar degradation (8). A rich cocktail of various volatile aldehydes absorbing in the UV region was also obtained by peroxodisulfate oxidation of sugars, aminoacids and alcohols (10).

During beer ageing the absorbance at 277 nm steadily increased although a small part of other UV absorbing compounds besides furfural was present. Recently we have suggested to use absorbance measurement at 220, 260 and 277 nm in the steam distilled wort and beer for brewing processes consistency checking up (7).

The absorbance measurement at isolated wavelengths is less time consuming than curve integration and more suitable to be automatized.

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2 Materials and Methods

2.1 Chemicals

Furfural (2-furanaldehyde) was obtained from Sigma Aldrich. After distillation at atmosphere pressure (b.p. 161 ºC) the stock furfural solution (c = 500 mg.l^{-1}) in 50 % (v/v) ethanol was prepared. The furfural content was confirmed by UV spectroscopy determination at 277 nm after diluting 1:100.

2.2 Instruments

- The SAN^{plus} segmented flow analyser (Skalar Analytical b.v. Breda, The Netherlands) equipped with distillation unit, quartz flow cell and 275 nm UV detector. Deionized water was used in the Skalar distillation unit.
- Quick steam programmable distillator 1-Cube, Czech Republic.
- Cadas 200 spectrophotometer with 1 cm quartz cuvette, Dr. Lange, Germany.

2.3 Procedures

2.3.1 Skalar analyser calibration

Stock furfural solution (c = 500 mg.l^{-1}) in 50 % (v/v) ethanol was diluted to get the range 0.2 – 1.0 mg.l^{-1} of furfural in deionized water for malt analyses or 5 % (v/v) ethanol for beer ones. Linear calibration curve was obtained for that range.

2.3.2 Furfural equivalent (FE) determination (Skalar)

Furfural standard solutions as well as samples were measured to get the Skalar detector response (DR). The furfural equivalent was computed by:

FE(µg.l^{-1}) = furfural standard conc. (µg.l^{-1}) x DR(sample)/ DR(standard).

2.3.3 Furfural equivalent (FE) determination (spectrophotometry)

Furfural standard solution (50 ml) as well as sample (50 ml) had been steam-distilled (approx. 2 min) until the same amount of distillate was collected. Absorbance at 277 nm was used instead of Skalar detector response and FE value computed.

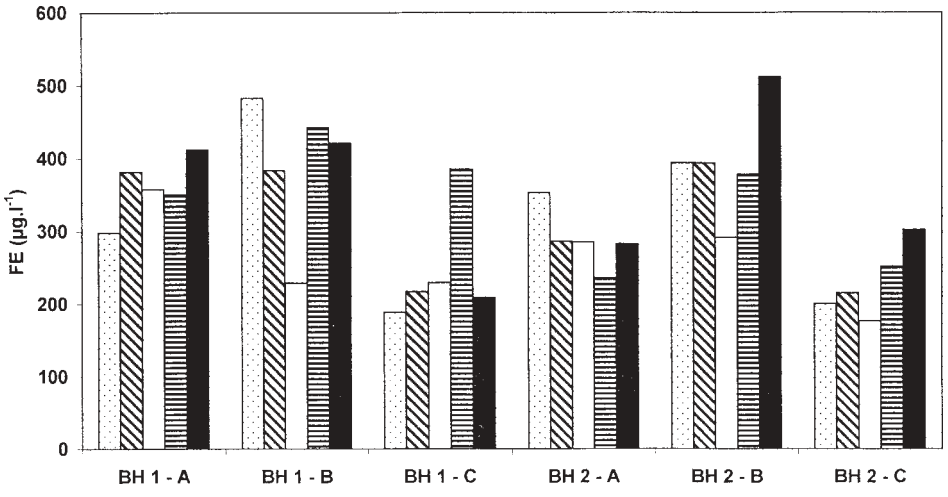

Fig. 1 The FE values (µg.l^{-1}) in hopped worts from two brewhouses (BH) using three different kinds of worts (A, B, C) within 5 brews

3 Results and discussion

3.1 FE values in Congress worts and hopped worts

The FE values of 20 samples of laboratory Congress worts varied between 40 – 60 µg.l^{-1}. Figure 1 shows FE values in cooled hopped worts from two experimental brewhouses using three different kinds of worts within five brews.

Certain differences witness a various degree of sugar degradation and Maillard reaction which might cause differences in volatile aldehyde composition. It has been mentioned in the literature that furfural content could be used as a suitable quality parameter of brewhouse process because of its quick and easy-to-make determination.

3.2 FE values in the course of main fermentation

Figure 2 shows the relationship between FE values and apparent degree of attenuation in the course of the main fermentation of beer (o.g.=12 %) taken from different fermentation vessels. The strong decrease of FE values in a short time after pitching confirms high yeast activity and good reduction power during the second part of the fermentation. The FE values increased a little after its initial reduction as well. The same tendency was observed in an earlier publication. The spectrophotometric measurement of the furfural reduction by yeast was a suitable method for yeast activity determination (10).

3.3 FE values during beer ageing

Three different kinds of beer were stored in the dark room at 20 °C. The FE values from different beer samples increased in a linear way with different slopes for each kind of beer. The same lager showed practically the same slope for the bottles or cans which is symbolize by one line for both containers (Fig. 3) The initial FE values were higher than usually published values for furfural content confirming the participation of other UV absorbing compounds. The average value of the slope for lager (8 µg.l^{-1}.week^{-1}) responds to the earlier found value (9).

3.4 Development rate of FE values at different temperature

Lager beer (o.g.=12 %), red wine, apple, orange and apricot commercial juices were stored in the dark at different temperatures. The FE values were determined and FE development rate measured (Table 1).

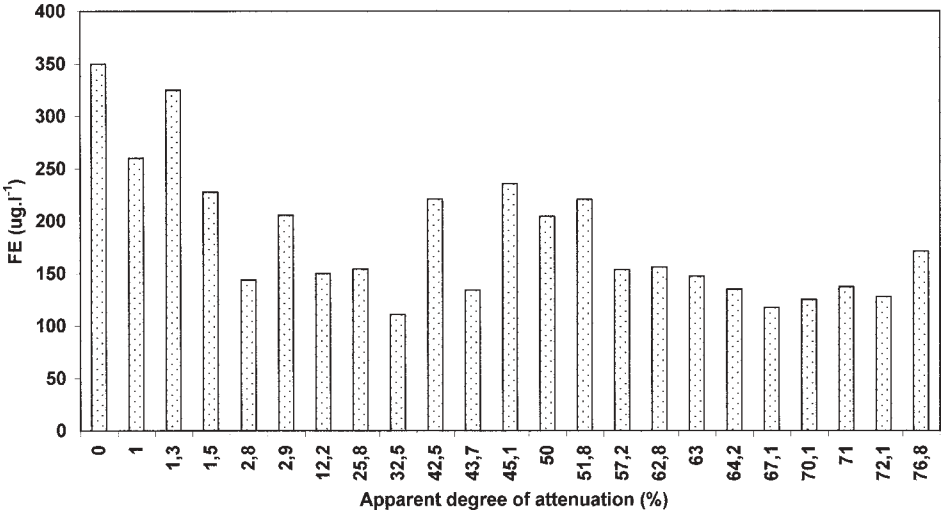

Fig. 2 The FE values in the course of lager main fermentation from different fermentation vessels

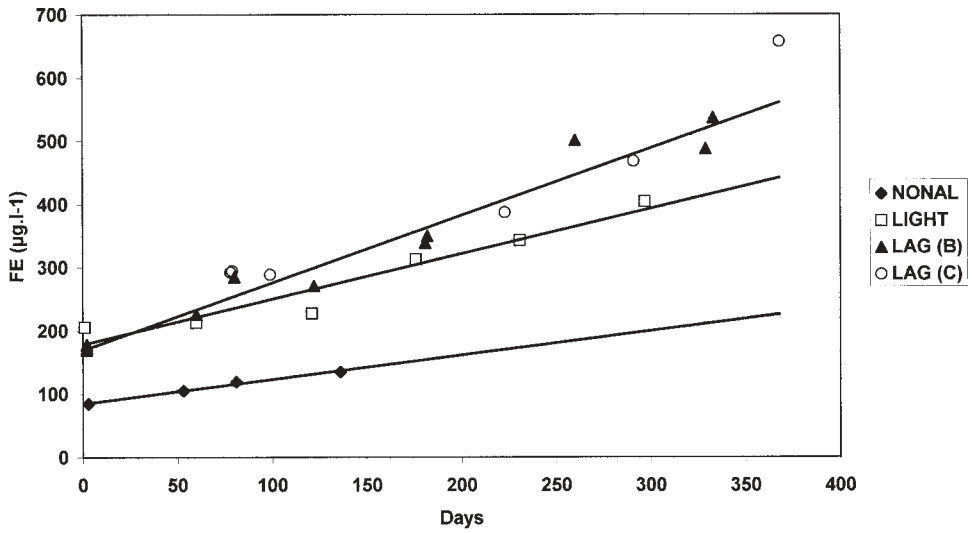

Fig. 3 The FE values during ageing of non-alcoholic beer (NONAL), light beer (LIGHT) and bottled (B) or canned (C) lager beer (LAG)

Table 1 Development rate of FE value at different temperature

Sample	FE value development rate (ug.l^{-1}.week^{-1})			
	6 ºC	28 ºC	37 ºC	45 ºC
Lager beer	4.3	6.5	78.2	211.6
Red wine	0.5	2.2	3.5	5.1
Apple juice	26.6	32.8	85.3	245.1
Orange juice	0.5	2.3	231	620.7
Apricot juice	60.6	102.7	1253	2123.3

4 Conclusion

- ❑ Flow distillation combined with UV detection can be used for furfural equivalent (FE) determination.
- ❑ Quick simple and automated determination enables high performance and highly reproducible analysis.
- ❑ No chemicals are needed which make the procedure highly ecological.
- ❑ The FE value is connected to sugar degradation associated with Maillard reaction and sensory active compounds formation during food and beverage deterioration.
- ❑ FE values can be used as a suitable indicator of brewhouse and fermentation processes consistency.
- ❑ Ageing of beer and fruit beverages can be checked up by FE value determination.

5 Zusammenfassung

Savel, J., und Pazourek, K.: Bestimmung des Furfural-Äquivalents (FE) beim Brauen — Monatsschrift für Brauwissenschaft 54, Nr. 11/12, 245 – 248, 2001

BC 35 Würze (Ausschlag- bzw. Anstellwürze)

Zur Bestimmung des Wertes für das Furfural-Äquivalent (FE) wurde ein Segmented-flow-Analysegerät der Firma Skalar verwendet, ausgerüstet mit Destillationseinheit, Quarzfließzelle und einem 275 nm UV-Detektor. Der FE-Wert beinhaltet das Absorptionsmaß sowohl von Furfural als auch von anderen flüchtigen Substanzen ausgedrückt als Furfuralkonzentration (µg.l^{-1}). Der FE-Wert hängt mit dem Zuckerabbau, der Maillard-Reaktion und der Bildung sensorisch aktiver Verbindungen während der Lagerung von Lebensmitteln und Getränken zusammen. Der FE-Wert kann außerdem als Indikator für die Konsistenz von Brauprozessen und zur Überprüfung der Alterung von Getränken verwendet werden.

Savel, J., et Pazourek, K.: Détermination de l'équivalent de furfural (EF) au cours de la fabrication de la bière — Monatsschrift für Brauwissenschaft 54, Nr. 11/12, 245 – 248, 2001

BC 35 Moût (moût fin cuisson, moût à l'entonnement)

On a utilisé un appareil analytique « segmented-flow » du type Skalar, équipé d'une unité de distillation, d'une cellule à flux continu en quartz et d'un détecteur UV à 275 nm pour la valeur d'équivalent de furfural (EF). La valeur EF comprend la mesure d'absorption du furfural et d'autres substances volatiles exprimée en concentration de furfural (mg.l^{-1}). La valeur de EF dépend de la dégradation des glucides, de la réaction de Maillard et de la formation de composés sensoriels actifs pendant le stockage de denrées alimentaires et de boissons. La valeur EF peut également être utilisée comme indicateur du bon déroulement du procédé de fabrication de la bière et pour l'examen du vieillissement des boissons.

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(Manuskripteingang: 31. 5. 2001)

EBC Standard Malt

The 15th Standard Malt has been accepted after analysis by the Analysis Committee of the European Brewery Convention. The malt can be used for checking the results of test methods described in Analytica-EBC or for calibration of apparatus (e.g. Friabilimeter) or other methods (flow injection, near infrared reflectance etc.).

Order

The order is to be sent to: Technical University of Munich , Chemisch-Technische Analyse, Weihenstephaner Steig 23, D-85350 Freising, Fax: +49-(0)-8161-71-4418, e-mail: cta@wzw.tum.de, or hagen@wzw.tum.de

Price

Price per tin (600 g): 15.00 Euro, plus charges for conveyance

Payment

Payment has to me made in advance by remittance order on receipt of the invoice to the account of Amtskasse der TU München, D-85350 Freising, Account No. 400 1001, Bank: HypoVereinsbank Freising, Bank Code: 700 211 80, Swift Code BV BE DE MM mentioning always: Order for EBC Malt and BKZ No. of the invoice. All bank charges to the debit of your account (AOR)

Shipment

On receipt of the amount immediate delivery (overseas export usually by air freight).

Results are shown in the table.

The repeatability value for wort colour visual by comparator (*) is given as an indication because repeatability cannot be estimated in the case of an interval basis measurement.

The figures of Friability+, Glassy Corns+ and Partly Unmodified Grains+ are based on the Friabilimeter Calibration Network (FCN).

Method 4.5.2: Extract Difference of Malt: Congress Mash has been archived.

Method 8.13.1: High Molecular Weight ß-Glucan Content of Wort: Enzymatic Method as well as Method 8.13.2: Fluorimetric Method are under research. The values will be published when the methods have been approved.

For each method, the following values were calculated:

- ❑ reference value
- ❑ tolerance (95% confidence level)
- ❑ repeatability (95% confidence level)

Values in brackets were obtained with small number of results and are only an indication.

This table should be used as follows to check duplicate results obtained when analysing the malt:

1. the difference between duplicates should be less than r_{95}

2. the mean result should lie within the range: reference value ± tolerance

For example, the measurement of Total Nitrogen % dry matter, the difference between duplicates should not exceed 0.036 % d.m. and the mean value should be 1.558 ± 0.061, that is between 1.497 and 1.619 % d.m.

		EBC Method	n	Reference value	Tolerance ±	Repeatability r_{95}
Moisture	%	4.2	31	4.15	0.36	0.17
Total Nitrogen	% dm	4.3.1	27	1.558	0.061	0.036
Extract Fine grind	% dm	4.5.1	30	81.98	0.94	0.43
Extract Coarse grind	% dm	4.5.1	27	80.02	0.24	0.47
Wort pH		4.18	28	6.01	0.14	0.04
Wort colour spectro	EBC units	4.7.1	22	3.26	0.94	0.25
Wort colour visual	EBC units	4.7.2	22	3.07	0.81	0.20 *
Boiled Wort colour	EBC units	4.7.3	20	5.62	0.93	0.35
Wort viscosity	mPa.s	4.8	25	1.523	0.057	0.017
Wort soluble N	mg/l	4.9.1	25	722	43	24
Wort soluble N	% dm	4.9.1	25	0.642	0.039	0.022
Kolbach Index	%	4.9.1	26	41.2	3.6	1.7
Wort FAN	mg/l	4.10	21	140	15	8
Wort FAN	% dm	4.10	22	0.125	0.013	0.007
Fermentability	%	4.11.1	19	80.9	2.5	0.6
Diastatic Power	WK/dm	4.12	17	240	55	15
α-Amylase	DU/dm	4.13	9	55.4	20.2	8.1
Modification	%	4.14	11	90.1	8.4	2.4
Homogeneity	%	4.14	10	75.7	15.7	7.5
Friability+	%	4.15	7+	82.4+	2.8+	2.6+
Glassy Corns+	%	4.15	7+	0.5+	0.4+	0.4+
Partly Unmod. Grains+	%	4.15	7+	2.6+	1.7+	1.5+
Total ß-Glucan fluo.	% dm	4.16.2	4	(0.55)	(0.05)	(0.04)

Note: Because of the risk of uptake of water and change of values once the tin has been opened an immediate use is recommended.