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AN APPLICATION OF ISO 5725 IN BREWING INDUSTRY

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The colloidal stability is very important part of the total beer quality. The stabilized beers have to have a long shelf-life. Determination of some haze forming complexes could be very useful for prediction of beer colloidal stability.

We study the repeatability and reproducibility of a method for determination of some haze forming complexes in beer. The method was tested in 10 laboratories. All of theme analyzed the same beer samples and carried out two measurements for each. Statistical evaluation of results was according ISO 5725 and previous experience. The applied ISO 5725 statistical analyzes ensured high quality and possibility of international recognition of the measurement method.

1. Introduction

The most important property of a measurement method is its accuracy. Evaluation the accuracy of the results of measurements and evaluation of the influence, which external factors have on the accuracy, are very important stages in developing and implementing methods for assessment beer quality. Among the major criteria for evaluation of beer quality are considered:

– Colloidal stability - long shelf-life;
– Haze forming complexes;

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– Prediction stability.

The objectives of this paper are to present the evaluating procedure of an adjusted method to measure colloidal stability based on alcohol chill haze test [4]. The evaluation of method's usability follows the requirements of the standard ISO 5725 [8].

2. The measurement method

Determination of alcohol chill haze in beer was introduced by Chapon and Chemardin [5]. The specially constructed apparatus consists of refrigerated nephelometer measuring the scattered light at 90° (Fig. 1) and plotter for registration of the nephelometric curves.

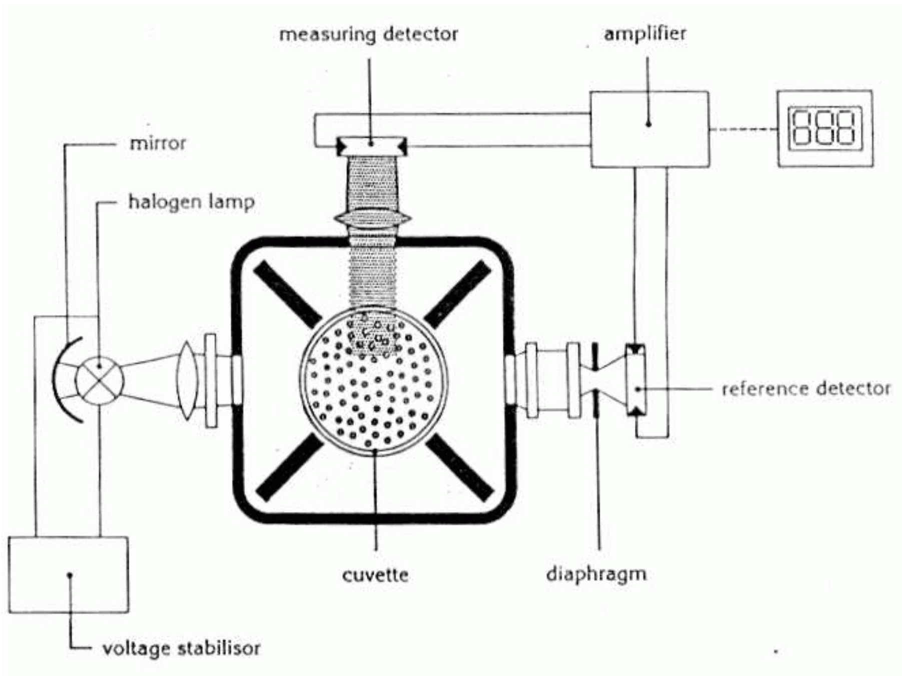

Figure 1: Principle of nephelometric mesurement: refrigerating and measuring the scattered light.

The effect of 1% alcohol addition to the beer is approximately equals to 1°C temperature decreasing. In the temperature interval -4°C to -8°C, 1°C temperature decreasing of beer is approximately equals to 1.5 EBC haze increasing. Chapon‘s nephelometer is not able to measure more than 20 EBC units haze.

There are modified versions of the alcohol chill haze test (see [1], [2], [3], [4], [5], [6], and [7]), which use different alcohol doses (reagent/beer ratio 3 to 6%), different temperatures (-4°C to -8°C) and different time of assay (40 to 100 minutes) .

Table 1 shows parameters of three methods for determination of beer alcohol chill haze.

Conditions	Chapon ([4], [5], [6])	Batchvarov et al.([2], [3])	IOB ([7])
Reagent	C_2H_5OH	C_2H_5OH	C_2H_5OH
Beer volume,ml	4	200	250
Reagent volume, ml	0.24	6	15
Ratio reagent/beer, %	6	3	6
Temperature, °C	-8	-5	-5
Time of assay, min.	40	40	60

Table 1: Determination of alcohol chill haze in beer three methods.

The Institute of Brewing (IOB) method [7] is not applicable for some non stabilized and normally stabilized beers (beers, with final turbidity greater than 10 - 12 EBC units). The method of consideration (Batchvarov et al. [3]) is characterized by 6 ml C_2H_5OH is added to 200 ml of degassed beer. The beer samples stay at -5°C for 40 minutes. The amount of alcohol chill haze is measured as an increase of the haze of the beer.

3. Experiment

Four stabilized and pasteurized beer samples with different alcohol chill haze levels were analyzed by 10 independent laboratories. Each laboratory process twice every sample according to the modified Chapon‘s alcohol chill haze test [3] and return the two measurements for each of the four beers. These results were obtained using nephelometers (haze meters) with 90° measuring angle, but with certain differences in measuring wavelength and geometry of the optical systems.

Statistical evaluation of results was performed according to ISO 5725 [8]. Our previous experience [9] in implementing this standard was instrumental in adoption of the data processing algorithms. The standard uses criteria ”repeatability” (within-laboratory-variance) and ”reproducibility” (total variance) to measure the quality of the given method. The term ”level” corresponds to brand of beer used in the experiment. Our experiment explores four brands of beers, each of the ten laboratories made 2 independent measurements for each beer. Or, in the

ISO 5728 terminology, we have an experiment of ten laboratories, four levels, with two observation in a cell. The data collected during the experiment are presented in Table 2.

Laboratory	Beer 1	Beer 2	Beer 3	Beer 4
1	0.43	1.40	5.15	9.18
1	0.45	1.35	5.03	9.07
2	0.40	1.53	4.65	8.64
2	0.38	1.47	4.57	8.48
3	0.66	1.62	5.09	8.81
3	0.58	1.82	5.86	8.88
4	0.43	1.69	6.60	9.74
4	0.50	1.73	6.73	9.67
5	0.38	1.80	5.76	9.65
5	0.42	1.75	7.02	9.48
6	0.39	1.20	3.92	7.60
6	0.32	1.63	4.15	7.34
7	0.58	1.30	4.30	7.41
7	0.63	1.39	4.18	7.75
8	0.37	1.41	5.15	9.06
8	0.40	1.17	4.75	9.08
9	0.45	1.60	3.09	6.37
9	0.45	1.50	2.60	5.95
10	0.54	1.74	5.05	8.90
10	0.46	1.69	5.33	8.70

Table 2: Results: Alcohol chill haze in Beer (EBC units).

4. Results and Discussion

The performed data processing was divided into three phases:

1. Outliers and strugglers
2. Precision
3. Relationship

Mandel‘s k and Mandel‘s h statistics to identify and exclude outliers are given in Fig. 2 and Fig. 3. Two outliers (laboratory 5 on level 3 and laboratory 6 on level 2) and one straggler (laboratory 9 on level 3) were detected by k statistics. The h statistic did not show outliers and stragglers. The detected outliers were excluded from the further analysis.

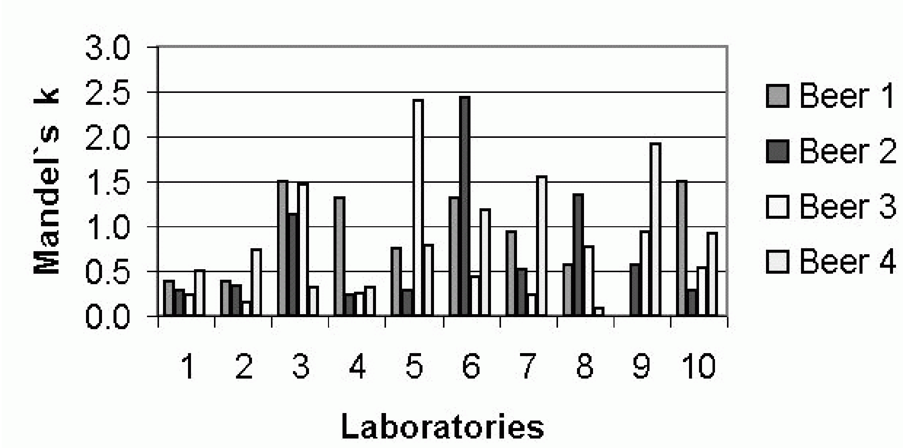

Figure 2: Mandel‘s within laboratory consistency statistic, k. The critical value for 5% (1%) confidence is 1.90 (2.32) when $n = 10$ and 1.90 (2.29) if $n = 9$.

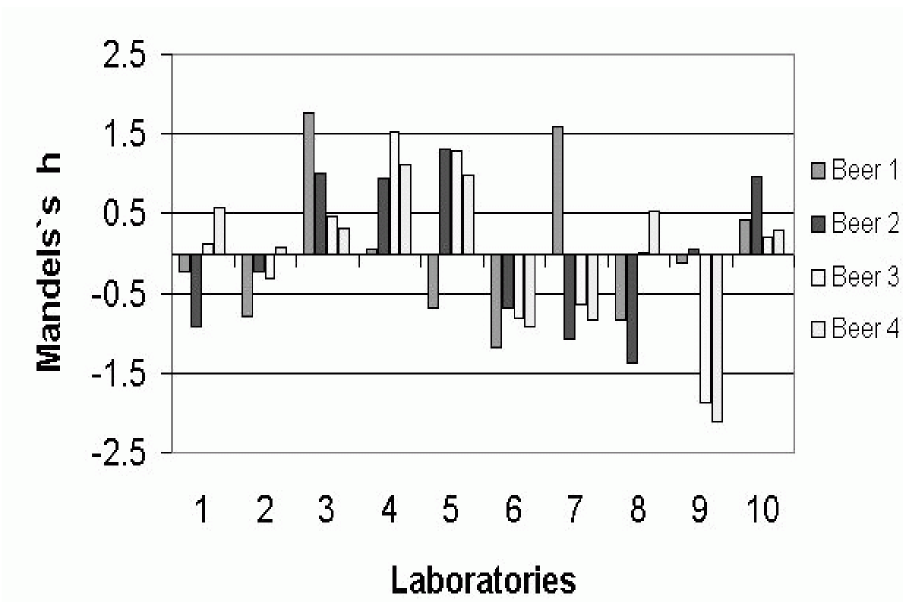

Figure 3: Mandel‘s between laboratory consistency statistic, h. The critical value for 5% (1%) confidence is 1.80 (2.22) when $n = 10$ and 1.80 (2.18) if $n = 9$.

The data for the precision of the measurement method are summarized in Table 3. It includes means, standard deviations (within, and between laboratory), coefficients of repeatability and reproducibility, and coefficients of variation (CV) of them.

Sample	Beer 1	Beer 2	Beer 3	Beer 4
Number of laboratory	10	9	9	10
Grand mean (m)	0.461	1.553	4.789	8.488
Repeatability standard deviation (Sr)	0.038	0.084	0.256	0.154
Reproducibility standard deviation (SR)	0.094	0.195	1.073	1.106
Repeatability (r95)	0.105	0.236	0.716	0.432
Reproducibility (R95)	0.264	0.545	3.004	3.096
CV of repeatability (CVSr)	8.17	5.44	5.34	1.82
CV of reproducibility (CVSR)	20.49	12.54	22.41	13.03

Table 3: Summary of the precision data (calculated from data of table 2).

The relationships are represented by the dependencies of repeatability and reproducibility standard deviations on the mean value. Three models of relationship are tested. Results are given in Table 4 and Table 5 correspondingly.

Multiple R	Relationship
0.331	$S_r = 0.027m$
0.632	$S_r = 0.070 + 0.017m$
0.907	$\log S_r = -2.734 + 0.580m$

Table 4: Relationship between repeatability standard deviation (S_r) and the mean (m).

Multiple R	Relationship
0.909	$S_R = 0.152m$
0.917	$S_R = 0.086 + 0.139m$
0.972	$\log S_R = -1.744 + 0.935m$

Table 5: Relationship between reproducibility standard deviation (S_R) and the mean (m).

In the both cases the logarithmic model were preferred.

5. Conclusions

The considered method for determination of alcohol chill haze (modified Chapon test) demonstrates acceptable repeatability and reproducibility.The method can be used to monitor the effectiveness of stabilization treatment and for prediction of the shelf-life of beer. A beer with a relatively low alcohol chill haze is expected to have a better colloidal stability than a beer with relatively greater one.

Application of the ISO 5725 statistical analyzes procedure ensured the international recognition of the above considerations.

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