

DETERMINATION OF TOTAL VICINAL DIKETONES IN BEER BY HEADSPACE CAPILLARY GAS CHROMATOGRAPHY

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The determination of total vicinal diketones in beer by the headspace capillary gas chromatography method of the Institute of Brewing Analysis Committee has been collaboratively tested by the members of the Analysis Committee of the European Brewery Convention. Two collaborative trials on three beer samples were performed in 14 laboratories. Repeatability (r_{95}) and reproducibility (R_{95}) values were obtained for 9 laboratories over the range of 20 to 90 μg . It was judged that reproducibility coefficients ranging after the second test from 32 to 94 were poor but it was decided that the method should nevertheless be included in the Analytica EBC as a guideline method with notice on its poor precision.

Key Words: Collaborative trial, beer (analysis method for), gas chromatography, diacetyl, pentanedione, total vicinal diketones (determination of).

INTRODUCTION

The current recommended methods of the European Brewery Convention for determining total vicinal diketones in beer rely on distillation followed by colorimetric analysis and packed column gas chromatography^{1,2}. In 1994, the Analysis Committee of the Institute of Brewing published a collaborative trial on the determination of vicinal diketones in beer by capillary gas chromatography³. In order to assess the suitability of the IOB method for the analysis of total diacetyl and total pentanedione in beer, the Analysis Committee of the EBC decided to collaboratively test the headspace capillary gas chromatography method for the determination of total vicinal diketones in beer.

EXPERIMENTAL

The organisation of the collaborative trials and the statistical treatment of the data were carried out according to the procedures given in the International Standard ISO 5725⁴. A uniform design was employed and two times three samples of beer covering the approximate range 20 to 100 $\mu\text{g/litre}$ of diacetyl were distributed to 14 laboratories. In order to overcome the decomposition of vicinal diketones precursors during the ageing of the beer, participants were requested to determine only total diacetyl and total pentanedione. In the second test the internal standard concentration has been lowered to 100 $\mu\text{g/litre}$ instead of 500 $\mu\text{g/litre}$ and the working range for calibration has been reduced to 0 to 200 $\mu\text{g/litre}$ instead of 0 to 250 $\mu\text{g/litre}$ to get linearity throughout the whole range. Between the two tests a ruggedness testing has been performed on internal standard concentration, injector temperature and detector temperature. Internal standard concentration has been shown to have a more significant effect than injector and detector temperatures. Twelve laboratories were involved in the first collaborative trial and 14 in the second.

RESULTS AND DISCUSSION

The raw data of the first test are presented in Table I for total diacetyl and Table III for total pentanedione. For diacetyl, one outlier was detected on samples A and B, and 3 on sample C according to the Dixon's Ratio Test for outliers at $p=0.01$ based on differences⁵. For pentanedione one outlier was detected on sample A, 2 on sample B and 3 on sample C according to the same Dixon's test.

A summary of the results of a statistical treatment of the data is given in Table II for total diacetyl and Table IV for total pentanedione. The precision values in terms of repeatability (r_{95}) and reproducibility (R_{95}) were calculated excluding the outliers. It was judged that for both total diacetyl and total pentanedione the number of outliers was too high and that the

TABLE I. Sample results for total diacetyl for the first trial concentrations in microgrammes/Litre

Laboratory	Beer samples					
	A		B		C	
1	50	50	10	10	50*	20*
2	70	60	30	30	30	30
3	61	65	32	32	27	29
4	41	38	32	33	32	33
5	103	93	43	44	40	37
6	40	40	15	14	38*	14*
7	155	166	8	6	16	12
8	119	128	20	21	20	20
9	57	59	33	29	29	28
10	202	213	7	6	6	4
11	27*	75*	17*	38*	12*	28*
12	32	34	12	11	11	11
Mean**	84	86	22	21	23	23
Grand Mean**	85		22		23	

* Outlier at $p=0.01$ based on differences

** Calculated excluding the outlier(s)

TABLE II. Summary of the statistical treatment for total diacetyl in the first trial

Sample Pairs	No of labs	Grand Mean	Repeatability			Reproducibility		
			Sr	cvr	r_{95}	SR	cvR	R_{95}
A	11	85	5.16	6.05	14.45	56.7	66.5	159.0
B	11	22	1.07	4.91	2.98	12.6	58.2	35.4
C	9	23	1.36	5.90	3.81	11.2	48.5	31.3

TABLE III. Sample results for total pentanedione for the first trial—concentrations in microgrammes/litre

Laboratory	Beer samples					
	A		B		C	
1	20	20	20*	10*	30	30
2	20	20	20	20	30	30
3	18	17	16	16	22	24
4	10	10	8	8	12	12
5	24	24	24	26	33*	37*
6	5	5	21	21	28*	23*
7	8	4	5	3	10	8
8	9	10	6	7	11	12
9	18	19	18	18	24	25
10	4	5	4	4	10	10
11	10*	43*	7*	24*	14*	25*
12	8	7	7	7	13	11
Mean*	13	13	13	13	18	18
Grand Mean**	13		13		18	

* Outlier at $p=0.01$ based on differences

** Calculated excluding the outlier(s)

TABLE IV. Summary of the statistical treatment for total pentanedione in the first trial

Sample Pairs	No of labs	Grand Mean	Repeatability			Reproducibility		
			Sr	cvr	r ₉₅	SR	cvR	R ₉₅
A	11	13	1.00	7.75	2.81	7.15	55.2	20.0
B	10	13	0.70	5.43	1.97	7.88	60.8	22.1
C	9	18	0.94	5.20	2.62	8.79	48.8	24.6

TABLE V. Sample results for total diacetyl in the second trial—concentrations in microgrammes/litre

Laboratory	Beer samples					
	A		B		C	
1	102	118	5	5	35	40
2*	50	55	11	12	14	14
3*	86	81	24	25	33	36
4	94	99	47	49	58	56
5	88	84	26	24	31	24
6	47	46	11	11	15	16
7	110	110	30	40	50	50
8*	67	71	21	21	26	27
9	91	99	28	31	41	37
10	67	55	14	12	18	18
11	151	132	36	35	45	47
12*	60	96	57	58	59	60
13*	62	55	14	13	17	19
14*	40	40	20	25	30	30
Mean*	88	87	24	26	36	36
Grand Mean**		87		25		36

* Laboratory which did not follow the requested method

** Taking in account only laboratories which did follow the requested method

TABLE VI. Summary of the statistical treatment for total diacetyl in the second trial

Sample Pairs	No of labs	Grand Mean	Repeatability			Reproducibility		
			Sr	cvr	r ₉₅	SR	cvR	R ₉₅
A	9	87	7.34	8.40	20.50	33.4	38.2	93.5
B	9	25	2.76	11.10	7.73	13.9	55.6	38.8
C	9	36	1.87	5.18	5.25	13.9	38.5	39.0

precision values were too poor particularly for the reproducibility. A second collaborative trial was then organised after a ruggedness testing.

Results for the second test were received from 14 laboratories. 9 participants followed the requested method with capillary column whereas 5 participants used different column or gas chromatographic conditions.

The raw data as received are presented in Tables V and VII. According to the Dixon's test, no outliers were detected for diacetyl results among the 9 laboratories which have followed the requested method and one was detected for the pentanedione results. A summary of the results of a statistical treatment of the data obtained from the 9 laboratories is presented in Table VI for total diacetyl and in Table VIII for total pentanedione. The obtained precision was as poor as it was in the first test, both for total diacetyl and total pentanedione.

CONCLUSIONS

Considering the poor precision values obtained in the two

TABLE VII. Sample results for total pentanedione in the second trial—concentrations in microgrammes/litre

Laboratory	Beer samples					
	A		B		C	
1	9	9	3	3	10	6
2*	9	11	6	6	7	8
3*	17	15	12	12	14	15
4	13	13	8	8	10	9
5	12	14	10	8	11	9
6	12	12	8	8	9	10
7	20	20	10	10	20	20
8*	20	18	14	12	13	14
9	7	9	7	6	9	8
10	12	10	7	8	8	8
11	25	21	16	16	18	18
12*	16	27	19	11	11	16
13*	10	8	7	8	8	8
14*	10	10	15****	20****	20	20
Mean*	13	13	8,6****	8,4****	12	12
Grand Mean**		13		8,5****		12

* Laboratory which did not follow the requested method

** Taking in account only laboratories which did follow the requested method

*** Outlier at p=0.01 based on differences for laboratories which did not follow the requested method

**** Calculated excluding the outlier

TABLE VIII. Summary of the statistical treatment for total pentanedione in the second trial

Sample Pairs	No of labs	Grand Mean	Repeatability			Reproducibility		
			Sr	cvr	r ₉₅	SR	cvR	R ₉₅
A	9	13	1.31	9.93	3.67	5.12	38.8	14.4
B	8	8.5	0.63	7.37	1.75	3.70	43.5	10.4
C	9	12	1.05	8.46	2.93	5.33	43.1	14.9

collaborative trials and particularly the unacceptable reproducibility values for both total diacetyl and total pentanedione, the Analysis Committee of the EBC judged not to accept the determination of total vicinal diketones in beer by headspace capillary gas chromatography as an official method. Nevertheless, due to the utility of the method, the Committee decided to include it in Analytica EBC as a guideline method.

REFERENCES

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