

DETERMINATION OF ANIONS IN BEER BY ION CHROMATOGRAPHY

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A method relying on ion chromatography, with suppressed ion detection, for the determination of anions in beer, has been collaboratively tested by members of the American Society of Brewing Chemists, the European Brewery Convention and the Brewery Convention of Japan.

Precision values obtained for the determination of chloride, sulphate and phosphate in beer were judged to be acceptable. Repeatability (r_{95}) and reproducibility (R_{95}) values for chloride were 5.7, 12.6, 12.5 and 15.0, 38.4, 36.8 respectively at corresponding mean levels of 68.7, 218.6 and 322.5 mg/litre. r_{95} and R_{95} values for sulphate were 7.5, 6.2, 7.6 and 44.8, 54.0, 46.5 respectively at corresponding mean levels of 101.4, 205.1 and 122.6 mg/litre. r_{95} and R_{95} values for phosphate were 14.1, 11.9, 24.9 and 78.7, 53.8, 84.0 at corresponding mean levels of 411.5, 224.1 and 397.5 mg/litre. Whilst the r_{95} value for nitrate was acceptable, the value for R_{95} was unsatisfactory.

The ion chromatographic method for determining chloride, sulphate and phosphate in beer is recommended for use and inclusion in ANALYTICA-EBC as an International Method.

Key Words: Anion (determination of), beer (analysis method for), chlorides (determination of), nitrate (determination of), phosphates (determination of), sulphates (determination of)

INTRODUCTION

The current methods recommended by the European Brewery Convention (EBC) for determining chloride, sulphate and nitrate are very labour intensive and are not readily automated⁴. In contrast, methods relying on ion chromatography, which are in use in many brewing laboratories, offer many advantages. The procedure requires little sample preparation and is both rapid and automated. Furthermore, it permits the measurement of many anions during a single chromatographic analysis. Anions of current interest are chloride, sulphate, nitrate and phosphate.

In 1992 the Analysis Committee of the EBC carried out a collaborative trial to test a method relying on ion chromatography, with suppressed ion detection, for determining anions in beer. From an examination of the resulting data, the precision values in terms of repeatability (r_{95}) and reproducibility (R_{95}) were judged to be unacceptable and, hence, the procedure was not put forward as a Recommended Method. In 1993, a collaborative study was organized by the American Society of Brewing Chemists (ASBC)², to test the ion chromatographic procedure published by Jancar *et al.*⁶. It was concluded from the results of this trial that the r_{95} values were acceptable for all anions except nitrate, and R_{95} values were acceptable for all anions, except nitrate and sulphate at low levels. It was decided, by the Sub-committee, to carry out a further trial, with a view to improving the reproducibility³. Moreover, it was suggested that the study should be concerned with more closely paired samples, which are stipulated in the split level design.

EXPERIMENTAL

The organization of the collaborative trial and the statistical treatment of the data were performed according to the Youden unit block experimental design¹, which is similar to the procedures given in the International Standard ISO 5725⁵. A split level design was employed and three sample pairs of beers were circulated to 15 laboratories. Participants were asked to determine the chloride, sulphate, nitrate and phosphate contents of the beers, to the nearest whole number (mg/litre), according to the circulated method relying on ion chromatography and suppressed ion detection. Chromatographic guard and analysis

columns, as supplied by DIONEX, were recommended for use in the trial, *viz* AG4A and AS4A respectively. However, participants were given the opportunity of using equivalent columns from other suppliers. In this trial, the Sub-committee comprised members of the ASBC, EBC and Brewery Convention of Japan (BCOJ).

RESULTS AND DISCUSSION

Results were received from 15 laboratories. Twelve laboratories followed the method according to Jancar *et al.*⁶, whereas 3 participants used a different column and eluting solvent.

The raw data, as received, are presented in Tables I–IV. Thirteen sets of data were identified as outliers and were rejected. One laboratory did not provide data for nitrate in one sample pair. Results for sulphate from one laboratory were excluded due to an apparent systematic error. A summary of the results of a statistical treatment of the data obtained for each anion is presented in Table V. Since only three pairs of samples were employed in the trial, it is not possible to determine reliably the dependence of r_{95} and R_{95} values on the levels of the anions.

TABLE I. Raw data as received for chloride (units mg/litre)

Laboratory	Sample Pair		Sample Pair		Sample Pair	
	A	B	C	D	E	F
1	64	60	198	213	347*	314*
2	67	68	220	221	330	320
3	70	70	205	224	315	311
4	69	69	241	243	358*	362*
5	69	67	213	225	305	315
6	77	74	194	192	252*	262*
7	77	73	245	243	357	362
8	72	72	228	231	324	326
9	66	66	216	220	313	318
10	65	68	210	212	315	314
11	62	62	212	212	318	317
12	79	71	219	225	323	321
13	66	61	212	219	321	328
14	62	62	209	218	324	326
15	76	77	271*	263*	312	325

*Rejected as outlier $p \leq 0.01$

TABLE II. Raw data as received for sulphate (units mg/litre)

Laboratory	Sample Pair		Sample Pair		Sample Pair	
	A	B	C	D	E	F
1	123	118	215	219	130	136
2	92	93	205	208	115	115
3	80	80	180	184	101	102
4	100	100	205	205	123	118
5	89	87	203	204	113	113
6	111	111	220	220	130	130
7	89	90	196	200	109	110
8	127	135	248	259	158	166
9	92	93	197	203	114	115
10	82	93	185	186	105	106
11	119	123	238*	231*	145	140
12	120	114	201	207	139	134
13	96	93	184	188	114	111
14	96	101	222*	211*	119	121

*Rejected as outlier $p \leq 0.01$

TABLE III. Raw data as received for nitrate (units mg/litre)

Laboratory	Sample Pair		Sample Pair		Sample Pair	
	A	B	C	D	E	F
1	21*	18*	9*	12*	18	16
2	11	12	8	8	12	13
3	10	10	8	8	11	12
4	17*	14*	10	8	18	16
5	10	9	9	8	11	11
6	11	11	12	11	14	15
7	20	20	8	8	12*	20*
8	12	13	13	12	14	16
9	9	9	7	7	11	11
10	10	10	9	9	14	14
11	8	8	7	7	10	10
12	12	12	10	10	14	14
13	19	18	17*	19*	20	19
14	7	7	—	—	11	11
15	13	13	12	12	15	16

*Rejected as outlier $p \leq 0.01$

TABLE IV. Raw data as received for phosphate (units mg/litre)

Laboratory	Sample Pair		Sample Pair		Sample Pair	
	A	B	C	D	E	F
1	391	369	202	207	351	371
2	390	386	214	214	352	368
3	433	434	236	237	424	427
4	395	389	202	204	374	380
5	440	430	245	245	420	400
6	431	424	213	219	399	393
7	378	380	206	204	352	372
8	435	437	243	242	418	417
9	363*	466*	159*	226*	434	463
10	416	407	241	229	395	395
11	448	445	238	241	428	426
12	402	393	220	212	388	379
13	393	379	209	212	381	390
14	396	378	208	207	371	376
15	465	459	270	256	438	444

*Rejected as outlier $p \leq 0.01$

TABLE V. Summary of precision data (units mg/litre)

	No of Labs	Mean	S_T	r_{95}	S_R	R_{95}
Chloride	15	68.7	2.0	5.7	5.4	15.0
	14	218.6	4.5	12.6	13.7	38.4
Sulphate	12	322.5	4.5	12.5	13.2	36.8
	14	101.4	2.7	7.5	16.0	44.8
Nitrate	12	205.1	2.2	6.2	19.3	54.0
	14	122.6	2.7	7.6	16.6	46.5
Phosphate	13	11.7	0.4	1.1	3.8	10.6
	12	9.2	0.5	1.3	1.9	5.4
Phosphate	14	13.8	0.8	2.3	2.9	8.0
	14	411.5	5.1	14.1	28.1	78.7
Phosphate	14	224.1	4.3	11.9	19.2	53.8
	15	397.5	8.9	24.9	30.3	84.0

CONCLUSIONS

The Analysis Committee of the EBC judged both the repeatability and reproducibility values for chloride, sulphate and phosphate to be acceptable. Therefore, the Committee has approved for inclusion in ANALYTICA-EBC the ion chromatographic method with suppressed ion detection for these anions. The method has been assigned International Status. Whilst the r_{95} value for nitrate was acceptable, the R_{95} was unsatisfactory and, hence, this anion was not included for recommendation. However, in view of the important role played by nitrate in brewing, the Committee decided to repeat the trial for this anion. It is envisaged that the reproducibility will be improved by including an aqueous solution of known nitrate concentration with the beer samples. In addition, particular attention will be given to the preparation of the calibration standards, detector sensitivity and data manipulation.

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