Determination of Sodium and Potassium in Beer

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CONCLUSIONS

Because of the limited amount of data, no firm conclusion can be made at this time. Nevertheless, the atomic absorption method shows promise.

The flame emission method with direct aspiration did not give satisfactory results.

RECOMMENDATIONS

1. It is recommended that the atomic absorption method using dilution and cesium chloride to be submitted for full-scale collaborative work.
2. Further Subcommittee work should be done to find adequate alternate methods.

The assignment given to this Subcommittee at the 1976 Annual Meeting was to evaluate methods for the analysis of sodium and potassium in beer. The literature was reviewed and the following comments were made.

Colorimetric and spectrophotometric methods are not very sensitive and, therefore, are not used to any extent (8). Indirect methods must be employed, such as the precipitation of the triple uranyl acetate of sodium and a bivalent metal, followed by the spectrophotometric determination of the uranyl ion.

Canales *et al.* (2) reported the determination of potassium in beer by turbidimetry. This method was not considered for collaborative work because it involved multiple pipetting and dilutions. The tetraphenyl-boro-sodium needed is fairly expensive.

Stone *et al.* (10) reported the determination of sodium and potassium by flame photometry in brewing materials. They used a "background" solution in preparing standards to correct for interference on the atomization of various factors such as surface tension, viscosity, and the presence of dissolved solids. This technique could be tedious, as beer dextrins have to be precipitated from beer with alcohol and dialyzed.

Frey (3) analyzed beer for sodium and potassium by atomic absorption. Samples were diluted 1:10 and the vapor discharge lamp was used. This type of lamp requires a special power supply because it is used at a current of approximately 900 mA. It was reported (7) that the vapor discharge lamps are not as stable as the hollow cathode lamps.

Moll *et al.* (6) determined potassium by atomic absorption using the hollow cathode tube. The beer was diluted 1:100 and cesium chloride was added to suppress ionization.

Sanui and Pace (9) reported that lanthanum is not as effective as cesium in suppressing ionization.

Heckman (4) reported on a collaborative study of sodium and potassium in feeds. With the limited number of assay results available, the atomic absorption technique appeared to give superior precision and more nearly theoretical recoveries of known additions of sodium than did the flame emission technique. Sodium values by atomic absorption were, without exception, lower by flame emission. The same was found for potassium, except for one sample.

During the summer, the method reported by Moll *et al.* (6) and a flame emission method were investigated. Although the latter gave a straight line calibration curve when dilution was used, a direct aspiration technique was considered because of its simplicity.

It was decided at the fall Technical Committee meeting to try the two methods in a small collaborative test. Unfortunately, it took longer than expected to gather results. One problem was the availability of the cesium chloride used in one method. Also, two laboratories had technical problems with their instruments. Thus, a full-scale collaborative test was not undertaken, limiting the amount of data available for satisfactory evaluation.

PROCEDURE

The atomic absorption method was organized in such a way that the same diluted samples could be used for both sodium and potassium analyses, since these elements are often determined

TABLE I
Determination of Sodium and Potassium in Beer
(Statistical Summary)

Element	Sample	Method	No. Labs	Grand Mean (x+y)/2 mg/l.	Within Lab Error (S_r) mg/l.	Between Lab Error (S_b) mg/l.	Total Lab Error (S_t) mg/l.	Coeff. Var. (S_t/G.M.)	Calc. F (S_t/S_r)	Critical F (95%)
K	pair 1	A.A.[a]	4	293.3	5.0	0	1.9	0.6	0.1	9.3
K	pair 2	A.A.	4	333.0	3.7	5.4	8.5	8.7	5.2	9.3
K	pair 3	A.A.	4	293.7	4.2	7.2	11.0	3.7	6.7	9.3
K	pair 1	F.E.[b]	3	315.0	2.4	51.9	73.5	23.3	900.0	n/a
K	pair 2	F.E.	3	324.0	7.4	34.7	49.6	15.3	45.5	n/a
K	pair 3	F.E.	3	292.0	15.1	14.6	25.6	8.7	2.9	n/a
Na	pair 1	A.A.	4	21.6	1.2	3.1	3.4	15.7	7.5	9.3
Na	pair 2	A.A.	4	53.0	2.4	3.7	5.8	11.0	5.8	9.3
Na	pair 3	A.A.	4	103.5	0.6	8.0	11.4	11.0	392.9	9.3
Na	pair 1	F.E.	4	26.3	0.6	3.1	4.4	16.8	47.7	9.3
Na	pair 2	F.E.	4	49.2	0.3	7.0	9.9	20.1	977.6	9.3
Na	pair 3	F.E.	4	97.4	2.2	17.3	24.6	25.3	126.4	9.3

[a]A.A. = Atomic absorption method.
[b]F.E. = Flame emission method.

simultaneously in beer. Thus, we used potassium standards which were ten times more concentrated than sodium standards. The standards were prepared in water and cesium was added at the concentration of 1000 mg/l. Cesium was also added to the diluted beer samples.

Easily ionized elements (such as the alkali metals) enhance the absorbance of other alkali metals because of ionization effects, the effects being greater at higher flame temperatures.

Apparently, the atoms of another easily ionized element provide additional electrons that cause some of the atoms of the first element to return to the ground state, thus causing an increase in absorbance. For example, this enhancement of the absorbance of sodium metal in the presence of potassium (and vice versa) can be eliminated by the addition of a suitable amount of another alkali metal, such as cesium (7,9).

In the flame emission method, direct aspiration was used and standards were prepared in water.

RESULTS AND DISCUSSION

Collaborator A submitted results from work done on a Pye Unicam instrument. He also submitted results of tests performed at a later date on a Perkin-Elmer instrument on loan; the results obtained using these instruments are indicated in the appropriate table.

Collaborator D did not use cesium chloride in the atomic absorption method. Sodium standards made up in beer known to be very low in sodium were used for the flame emission methods. For potassium, standards were prepared in a solution containing ethanol, gelatin, phosphoric acid, and sucrose. This solution is designed to give standards that have the same flow characteristics and luminosity as the beer sample which is aspirated directly into the burner. Also, only one sample of each pair was reported. For these reasons, the results of Collaborator D were not included in the statistical analysis.

Because of the limited number of collaborators, the calculations for identification of outliers are doubtful; therefore, all results were included in the analysis. The statistical summary is shown in Table I and Table Ia and the results in Table II.

The Grand Means and the t-test do not indicate a major difference between the two methods.

On the other hand, the total lab error (S_t) is much greater with the flame emission technique for both sodium and potassium. The between-lab error (S_b) is the major contributor to the total lab error. This is also shown by the calculated F.

This could be explained by the fact that the atomic absorption method gives straight or near straight standard curves, whereas, with flame emission, the standard curves are nonlinear and vary greatly from one laboratory to the other (see Figs. 1 and 2).

The coefficient of variation (S_t/G.M.) changes drastically from one sample pair to the other for the analysis of potassium. This is true for both the atomic absorption and the flame emission procedures. This could be caused by the fact that values of Collaborator B are much higher than the average on some samples and that the results of the two samples of a pair differ much more than those of other collaborators.

Collaborator B had an instrument failure and had to do the Subcommittee work on an unfamiliar substitute instrument.

The coefficients of variation for sodium are more uniform, but higher, for the flame emission method.

In the last Beer Analysis Check Service (1), sodium analysis was included. Eleven laboratories submitted data for sodium, most of those using atomic absorption. Disregarding two outliers, the results were:

Average	72.8 mg/l.
Standard deviation	4.97
Maximum	80.5
Minimum	65.8
Coefficient of variation	6.8

It appears that, with the atomic absorption method using cesium chloride, we can improve the precision of the analysis.

Comments

Following are some of the subcommittee members' comments in regards to avenues of investigation:

TABLE Ia
Testing for Difference between the Two Methods

Element	Pair No.	t	Critical t
K	1	−0.61	>3.0
K	2	0.37	>3.0
K	3	0.06	>3.0
Na	1	−1.69	>3.0
Na	2	0.66	>3.0
Na	3	0.45	>3.0

TABLE II
Determination of Sodium and Potassium in Beer
(Results in mg/l.)

		Atomic Absorption						Flame Emission					
		Sample 1		Sample 2		Sample 3		Sample 1		Sample 2		Sample 3	
Lab. No.	Element	A	B	A	B	A	B	A	B	A	B	A	B
A[a]	K	295	292	325	335	290	285	285	285	300	305	285	285
A[b]	K	295	295	330	330	290	285	...	...	...	...	...	...
B	K	300	285	338	346	300	307	378	372	372	357	295	332
C	K	292	292	330	330	295	298	285	285	305	305	280	280
D[c]	K	315	...	350	...	300	...	320	...	325	...	320	...
A[a]	Na	20.0	21.0	53.5	52.5	109	108	30.0	29.0	58.0	59.0	120	127
A[b]	Na	21.0	18.5	49.5	49.0	98	99	22.0	22.0	42.0	42.0	87.0	87.0
B	Na	25.1	25.1	55.5	62.0	112	112	27.0	26.2	49.3	50.0	89.5	92.4
C	Na	20.3	21.7	50.0	52.0	95	95	26.5	27.5	46.2	46.5	88.0	89.0
D[c]	Na	23.0	...	52.0	...	98	...	30.0	...	53.0	...	87.0	...

[a]Results with Pye Unicam instrument.
[b]Results with Perkin-Elmer instrument.
[c]Results of Collaborator D not used in statistical analysis.

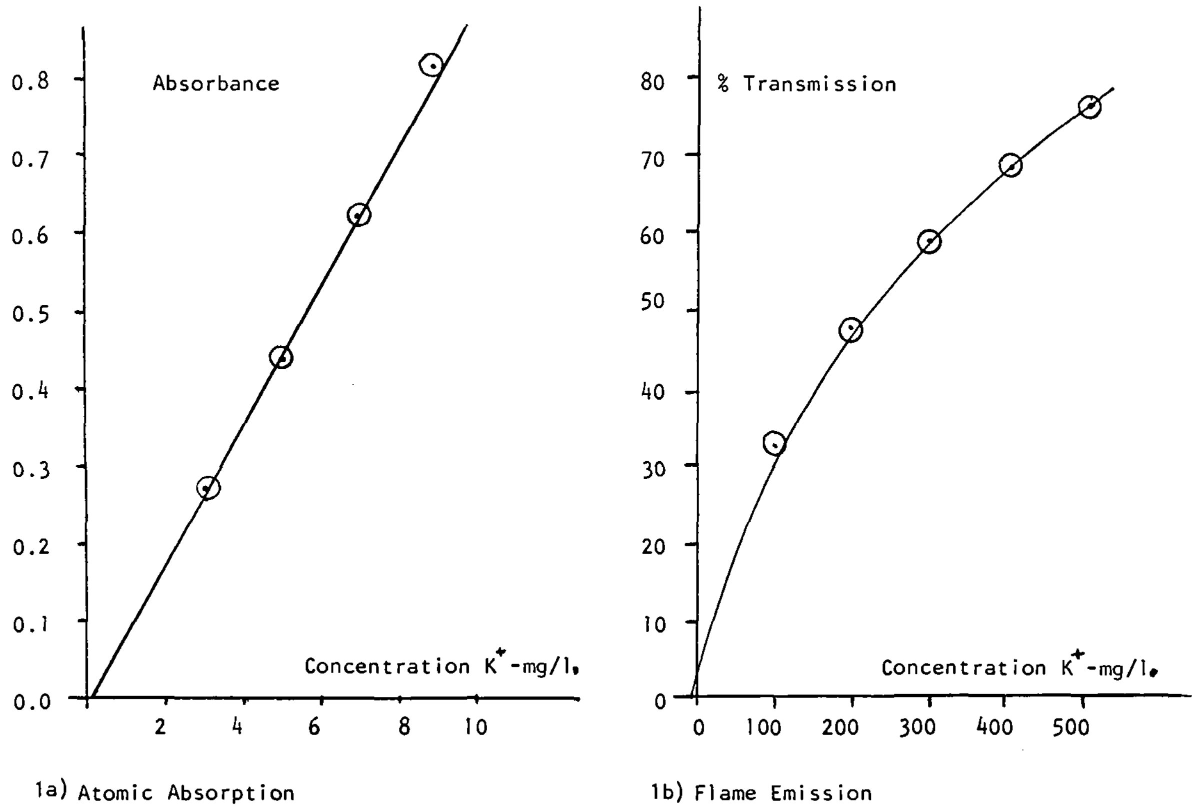

Fig. 1. Determination of potassium in beer (standard curve).

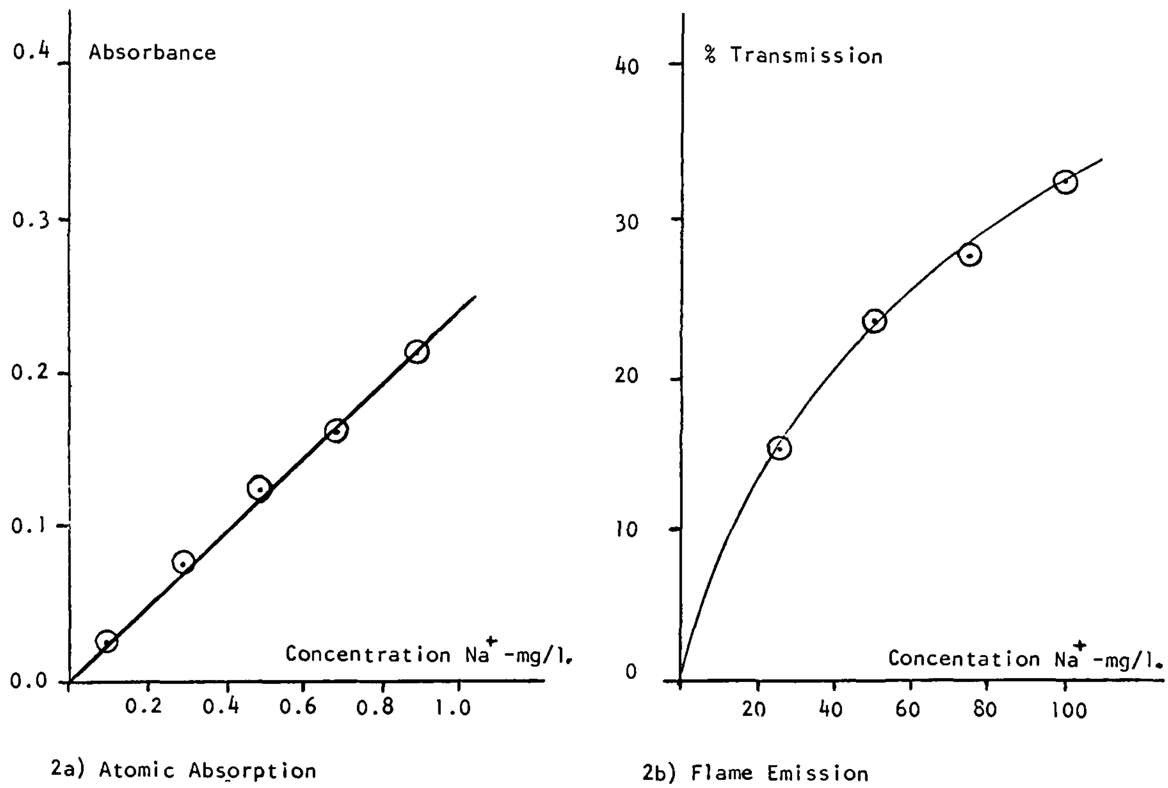

Fig. 2. Determination of sodium in beer (standard curve).

1. With atomic absorption, a beer standard addition for calibration should be tested. One has to have a beer with a low concentration of the element sought and the standard curve has to be linear to extrapolate.
2. The use of a less sensitive resonant line for atomic absorption analyses at reduced sensitivity is suggested to avoid the need for dilution. Argon-filled hollow cathode lamps are preferred in this case since Neon has strong emission lines in the vicinity (5).
3. The drawback of having to dilute the sample could be minimized if the procedure is automated by the use of the autoanalyzer system. This could reduce the errors of pipetting and could reduce the amount of cesium chloride needed.
4. The use of selective ion electrode should be investigated.
5. A straight line calibration curve could be obtained if dilution is used in flame emission.
6. Better sensitivity could be obtained if a proper ratio of dilution is used along with the proper concentration of standards.

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