

Determination of Chloride in Beer

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Key words: *Conductometric, Electrode, Mercurimetric, Potentiometric.*

CONCLUSIONS

The new method, using a silver ion specific electrode to follow a silver nitrate titration of chloride ion, gave very satisfactory results. The coefficient of variance of combined errors was 4%, and the reproducibility was excellent. The collaborators expressed a definite preference for this potentiometric method over the conductometric method. Both the potentiometrically and the conductometrically monitored titrations gave statistically equivalent chloride values, but the former was superior both in reliability and simplicity.

RECOMMENDATIONS

1. Three chloride methods—potentiometric titration, conductometric titration, and mercurimetric titration—should be considered for adoption and inclusion in the Beer chapter of ASBC "Methods of Analysis."
2. The subcommittee, having completed its assignment, should be discharged.

The subcommittee previously evaluated the methods set forth by the European Brewery Convention (*EBC*) (3). The mercurimetric method, as proposed by the *EBC*, gave erroneously high chloride values. A cation exchange treatment step was implemented (1), after which the results conformed to those obtained by other methods. The modified mercurimetric method gave very good reproducibility, but it suffered from significant variances between laboratories because of operator interpretation of the subtle

endpoint color change.

The conductometric method gave higher within-laboratory errors but very low between-laboratory errors and acceptable combined errors.

In the present study, we attempted to reduce the random variance of the conductometric method and to evaluate a silver specific ion electrode in a potentiometric titration.

PROCEDURE

The present potentiometric titration is based on work reported by Preen and Woodward (5) and Hubach (4) and on unpublished work in the chairman's laboratory. The beer sample is acidified with nitric acid then titrated with silver nitrate. The silver electrode develops a potential that increases with the log of the silver ion concentration, which increases dramatically at the endpoint.

The conductometric method was repeated with the stipulation that the sample should not be diluted any more than necessary to cover the electrode assembly. The conductance was plotted after incremental additions of AgNO_3 titrant.

We had a limited number of collaborators; to increase the reliability of statistical treatments, each collaborator received **sample pairs of three different lager beers, which covered a broad range of chloride concentration (70–200 mg/L).** The design followed the Youden Block concept (6).

RESULTS AND DISCUSSION

Results are presented in Table I and statistical treatment of these data is summarized in Table II. For the potentiometric method, variances are well within the acceptable range for a test of this nature. The high F values for pairs 1 and 3 are a consequence of the very low within-laboratory errors (S_w). Although the between-laboratory errors (S_b) are significantly higher, they are still acceptable. The average coefficient of variation of the combined errors for the three pairs is less than 4%. This is particularly impressive because most of the collaborators had no previous experience with silver ion specific electrodes.

TABLE I
Determination of Chloride in Beer^a

Lab.	Pair 1				Pair 2				Pair 3			
	A ^b		B ^c		A		B		A		B	
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
1	72	72	71	69	91	95	103	103	194	208	195	213
2	68	70	122	112	201	218
3	90	80	120	110	210	220
4	70	69	68	67	101	102	100	100	193	209	190	208
5	75	80	100	100	180	200
6	76	72	112	108	196	216
7	64	64	72	68	96	97	114	104	163	199	180	196
8	78	76	116	111	198	221
9	72	72	68	70	104	110	104	112	204	210	200	216
10	70	70	103	104	194	212
11	73	61	68	64	97	110	104	102	190	207	192	208
12	67	64	105	106	196	206
Means	74	72	70	68	105	105	106	105	193	210	193	209

^a mg/L.^b Conductometric method.^c Potentiometric method.

TABLE II
Determination of Chloride in Beer: Statistical Summary

Method ^a	Sample Pair	No. of Labs.	Grand Means ^b	Error			c.v. ^c (%)	Calculated F ^c	Critical F ^f
				Within-Lab. ^c	Between-Lab. ^c	Combined ^d			
A	1	9	73	3.9	5.8	6.9	9.5	5.4	3.44
	2	9	105	5.3	7.6	9.3	8.8	5.1	3.44
	3	9	201	6.2	9.7	11.5	5.7	5.9	3.44
B	1	8	69	1.6	2.5	2.9	4.2	6.1	3.79
	2	8	105	3.6	2.4	4.3	4.1	1.9	3.79
	3	8	201	2.1	5.9	6.3	3.1	16.8	3.79

^a A = Conductometric method, B = potentiometric method.^b Grand mean = GM = $(\bar{X} + \bar{Y})/2$.^c Calculated per Youden and Steiner (6).^d Combined error (S_c) calculated from within-lab. error (S_r) and between-lab. error (S_b); $S_c = \sqrt{S_r^2 + S_b^2}$.^e Coefficient of variation of $S_c = c.v. = 100(S_c/GM)$.^f Critical F from tables of F distribution (2) at $P = 0.05$.

An added advantage of the potentiometric titration is that the tedious plotting of all the data points is not necessary. The endpoint can be determined by inspection for the increment of greatest change, or by differential plotting, or by titrating to a preestablished endpoint potential. In the current study, all three of these treatments gave results statistically equivalent.

The results of the conductometric method not only have higher error values than does the potentiometric test, but also higher error values than the corresponding conductometric results from last year's program (1). The coefficient of variation of combined error is 8% in the present study, as opposed to 6% in the previous program. Apparently the more concentrated beer sample used here had a detrimental effect on the precision of the results.

Table III shows the average coefficients of variation for the three methods tested by this subcommittee during the past two years. The absolute errors are expressed as a percentage of the grand mean, and the results of the three different sample pairs are averaged. This table demonstrates that the potentiometric method has the least combined and random error. The conductometric method has low between-laboratory error but higher random error. The mercurimetric test has acceptable random error but much higher between-laboratory error.

TABLE III
Average Coefficients of Variation (%) of Errors for the Three Methods^a

Method	No. of Labs.	Error		
		Within-Lab.	Between-Lab.	Combined
Potentiometric	8	2.3	2.9	3.8
Conductometric	7	5.4	2.3	6.0
Mercurimetric	10	4.0	9.0	10.1

^a Average result of the three sample pairs. Conductometric and mercurimetric results are taken from the 1979 report (1).

LITERATURE CITED

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APPENDIX BEER CHLORIDE

The recommended methods consist of titrating the available chloride ions and detecting the presence of the titrant cation that exists uncomplexed in solution after the endpoint. Excess AgNO_3 titrant can be detected by conductivity determination, or the free Ag^+ ion can be detected by an ion specific electrode. With $\text{Hg}(\text{NO}_3)_2$ titrant, the free Hg^{+2} ion can be detected by its colored complexation product with an indicator.

A. POTENTIOMETRIC TITRATION (Reference Method)(2,4,5)

Reagents

- (a) *Silver nitrate*. Add 4.79 g of AgNO_3 to 1 L of deionized water. (1 ml \approx 1 mg Cl^-) Protect the reagent from light.
- (b) *Sodium chloride*. Add 1.648 g of NaCl to 1 L of deionized water. (1 ml = 1.00 mg Cl^-)
- (c) *Nitric acid*, concentrated.

Apparatus

- (a) *pH meter*, with millivolt mode and ± 1 mv reliability.
- (b) *Beaker*, 50-ml.
- (c) *Pipets*, 0.5-ml, 3-ml, and 25-ml.
- (d) *Buret*.
- (e) *Stirrer*, magnetic, electric or air driven.
- (f) *Silver ion sensing electrode*. If a combination electrode is not used, a suitable reference electrode is necessary. This should be nonclogging and should not have chloride ion in the filling solution.

Calibration

Add enough deionized water to a 50-ml beaker to cover the tips of the electrodes. Add 3.0 ml of chloride standard and 0.5 ml of concentrated HNO_3 . Provide continuous stirring. With the meter in the mv mode (or the + mv mode), use the calibration control to obtain an on-scale reading. Any starting potential is satisfactory. Record the value, to the nearest mv, when the reading is stable. Recording the potential after each addition, add the silver nitrate titrant in 0.5-ml increments. Near the endpoint (where the mv readings change rapidly), add 0.2-ml increments. After the endpoint, add 0.5-ml increments until at least 2 ml of excess titrant has been added.

Method

Pipet 25 ml of attemperated degassed beer into a 50-ml beaker. If necessary, add deionized water to cover the electrode tips. Add 0.5 ml of concentrated HNO_3 and provide stirring. Proceed with titration as described under "Calibration."

Calculations

Determine the endpoint of the titration by one of the following methods.

1. Plot mv vs ml of titrant and draw a smooth S-shaped curve through the points. The inflection point of the curve is the endpoint.

2. By inspection, determine the increment having the greatest change in instrument reading per unit addition of AgNO_3 . If the exact endpoint cannot be determined by inspection, plot a differential titration curve, showing the change in mv for equal increments of AgNO_3 against the volume of AgNO_3 at the midpoint of that increment. The apex of this curve is the endpoint.

Determine the concentration of chloride ion.

$$1 \text{ ml AgNO}_3 = 3/S = F \text{ mg chloride}$$

in which S = ml of titrant at endpoint of calibration titration.

$$\text{Chloride in beer (mg/L)} = T \times F \times 40$$

in which T = ml of titrant at endpoint of beer titration.

Example

3.09 ml of AgNO_3 in titration of 3 ml of standard.

1.9 ml at endpoint of 25 ml of beer titration.

$$F = 3/3.09 = 0.97.$$

$$\text{Cl (mg/L)} = 1.9 \times 0.97 \times 40 = 74 \text{ mg/L.}$$

B. CONDUCTOMETRIC TITRATION (Alternate Method)

Reagents

- (a) *Silver nitrate*. Add 4.79 of AgNO_3 to 1 L of deionized water. (1 ml \approx 1 mg Cl^-). Protect the reagent from light.
- (b) *Sodium chloride*. Add 1.648 g of NaCl to 1 L of deionized water. (1 ml = 1.00 mg Cl^-).

Apparatus

- (a) *Conductivity meter*, and dip type cell with platinum electrodes.
- (b) *Beaker*, large enough to allow total immersion of the electrode surfaces.
- (c) *Pipets*, 3-ml and 25-ml.
- (d) *Buret*.
- (e) *Stirrer*.

Calibration

Add 3.0 ml of the sodium chloride standard to enough deionized water to completely cover the electrode surfaces. Provide agitation either by manually stirring the cell assembly or with a stirrer. Be certain that the solution in the electrode housing is in equilibrium with the outer solution. Add silver nitrate in 0.25-ml increments, recording the conductance after each addition. The conductance decreases gradually until the endpoint and then increases. Continue the titration until 1.5 ml has been added after the endpoint.

Method

Pipet 25 ml of room temperature degassed beer into a beaker with at least 25 ml of deionized water, or enough to cover the cell. Proceed with the titration as described under "Calibration." With prolonged use, the electrodes may require cleaning due to the deposit of precipitates from the titration. Depending on the cell characteristics, fluctuating readings may occur with beer. Usually, a cell with a higher cell constant, further dilution, or addition of ethanol will retard the fluctuation.

Calculations

Plot the conductance vs volume of titrant. Construct the best two straight lines through the descending and ascending points. The intersection of these lines is the endpoint volume.

$$1 \text{ ml AgNO}_3 = 3/S = F \text{ ml chloride}$$

in which S = ml of titrant at the endpoint of the calibration titration.

$$\text{Chloride in beer (mg/L)} = T \times F \times 40$$

in which T = ml of titrant at the endpoint of the beer titration.

Example

3.09 ml of AgNO_3 endpoint in 3.0 ml of standard titration.

1.9 ml AgNO_3 endpoint in 25 ml of beer titration.

$$F = 3/3.09 = 0.97.$$

$$\text{Cl (mg/L)} = 1.9 \times 0.97 \times 40 = 74 \text{ mg/L.}$$

C. MERCURIMETRIC TITRATION (Alternate Method)

Reagents

- (a) *S-diphenylcarbazone*, 0.5% in ethanol (95%), store in dark.
- (b) *Xylene cyanole FF*, 0.1% in ethanol (95%), store in dark.

- (c) *Nitric acid*, 10% concentrated HNO_3 in deionized water.
- (d) *Mercuric nitrate*, dissolve 4.90 g of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 1 L of deionized water. Include 1 ml of concentrated HNO_3 as a stabilizer.
- (e) *Sodium chloride*. Add 1.648 g to 1 L of deionized water. 1 ml = 1.00 mg of chloride.
- (f) *Strong acid cation exchange resin*, H^+ form. Wash thoroughly with deionized water. (See Note).
- (g) *Sodium hydroxide*, 5%.

Apparatus

- (a) *Pipets*, 0.1-ml, 1-ml, 3-ml, and 25-ml.
- (b) *Buret*.
- (c) *Erlenmeyer flasks*, 125-ml.
- (d) *pH meter*.
- (e) *Stirrer*.
- (f) *Filter paper* (fast), and funnel.

Calibration

Pipet 3.0 ml of sodium chloride standard into a 125-ml Erlenmeyer flask and add about 50 ml of deionized water. Add 1 ml of indicator (reagent a) and 0.1 ml of indicator (reagent b). Adjust the pH to 2.9 (make sure the electrode does not leak chloride). Titrate with $\text{Hg}(\text{NO}_3)_2$ until a slight purple color persists.

Method

Pipet 25 ml of degassed beer into a 125-ml flask. Add a few grams of cation exchange resin (either as a powder or a slurry). Mix with a stirrer for 5 min, then filter into a clean 125-ml flask. Wash the original flask, resin, and filter paper with approximately 25 ml of

deionized water, combining the rinse with the previous filtrate. Add indicators, adjust pH, and titrate as described in "Calibration."

Note

Before using the resin, verify that it is chloride free by running a deionized water sample in place of the beer sample. If an appreciable titer value results, the resin wash must be repeated.

Calculations

$$1 \text{ ml Hg}(\text{NO}_3)_2 = 3/S = F \text{ mg chloride}$$

in which S = ml of titrant used in calibration titration.

$$\text{Chloride in beer (mg/L)} = T \times F \times 40$$

in which T = ml of titrant used in titration of 25 ml of beer.

Example:

3.10 ml of $\text{Hg}(\text{NO}_3)_2$ at endpoint of 3.0 ml of standard titration.

1.9 ml of $\text{Hg}(\text{NO}_3)_2$ at endpoint of 25 ml of beer titration.

$$F = 3/3.1 = 9.7.$$

$$\text{Cl (mg/L)} = 1.9 \times 9.7 \times 40 = 74 \text{ mg/L.}$$

References

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