

# Automated Determination of Chloride Concentration in Wort and Beer<sup>1</sup>

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## ABSTRACT

The objective of this study was to evaluate an automated coulometric titration method for the determination of chloride ( $\text{Cl}^-$ ) and compare it to the results obtained with a potentiometric titration reference method. The coulometric titration method provided slightly higher chloride readings than found with the potentiometric procedure; however, the correlation coefficient between the two methods was 0.989 for wort and 0.994 for beer. Both methods provided excellent results, with the coulometric procedure requiring one third the time and being easier to perform. The coulometric method also required minimal instrument setup, standardization, and sample preparation and used very stable reagents.

Key words: *Automation, Beer, Chloride, Coulometric, Titration, Wort*

Several methods have been accepted by an ASBC subcommittee (1) for the determination of chloride in beer. Of those, a potentiometric titration procedure (1,5,6) is recommended as a reference method, with conductometric and mercurimetric titration procedures as alternate methods. An additional alternate procedure would appear to be coulometric titration, especially as presently automated (2). The coulometric method has been used extensively in clinical laboratories and has provided excellent data on chloride concentrations in biological fluids (3,4).

The coulometric titration is performed by passing a fixed current between a pair of sensing electrodes. The anode, a silver wire, is consumed in the reaction, releasing silver ions into solution. As automated (2), the instrument registers the equivalence point and automatically converts the chloride concentration to milliequivalents/L, which, when multiplied by 35.5, the equivalent weight of  $\text{Cl}^-$ , gives mg/L of chloride.

## EXPERIMENTAL

### Recovery

For recovery determinations, known amounts of NaCl were added to wort and to beer that had been previously analyzed by both the potentiometric titration method (1) and the automated coulometric titration procedure. These "spiked" samples were then analyzed by the same two methods and percent recoveries determined. In addition, a series of domestic beers was analyzed by both methods, and results for chloride concentration were compared.

### Coulometric Titration

**Apparatus.** A Buchler Chloridometer, model 4-2500 and vials for the above (20 × 40 mm, Buchler 4-2018) were used. Other equipment included pipets (1, 2, and 3-ml, class A), a rinse bottle for distilled water, volumetric flasks (500 ml), graduated cylinders (25 and 250 ml), and a sonic bath for degassing.

**Reagent.** For the chloridometer acid reagent, 250 ml of distilled water was added to a 500-ml volumetric flask. Concentrated nitric acid (12.0 ml) and glacial acetic acid (200 ml) were then added and the mixture made to volume.

**Procedure.** With the instrument off, we made sure that the silver electrode was the same length as the other electrodes and thicker than the shaft of an ordinary pin. If it was not, we snipped off the

old segment and drew the wire off the spool until the silver electrode was as long as the others. The silver wire was tightened in the binding post only enough to make good contact. (The wire was not put through the hole in the binding post as this would deform the wire.)

The beer sample, or samples were degassed by sonicating.

The electrodes were cleaned by filling a 20 × 40-ml vial with decarbonated beer and immersing the electrodes in the beer for 15 sec with the stirrer on. The electrodes were rinsed with distilled water from the wash bottle and wiped dry. This cleaning step was used between each sample, which made unnecessary the cleaning with silver polish suggested by the manufacturer's manual (2).

The chloridometer was set to "low range" and "auto titration," and 1 ml of chloridometer acid reagent and 3 ml of distilled water were pipetted into each of three vials. These three were read as blanks, and the average blank value was entered into the "blank adjust" on the front of the instrument.

Acid reagent (1 ml) and distilled water (2 ml) were pipetted into each of three vials, and then 1 ml of a sample of degassed beer or wort was pipetted into each of the vials. Values for each vial were read and recorded. The electrodes were rinsed and wiped between each reading and cleaned as above between each sample (one set of three vials).

After all readings were completed, the unit was stored with the electrodes immersed in distilled water.

**Calculations.** Calculations were made using the formula

$$\frac{\text{Average of three values}}{100} \times 35.5 = \text{Cl}^- (\text{mg/L})$$

Results were reported to the nearest milligram per liter.

The unit is designed to read in milliequivalents of chloride per liter with a 10-ml sample. We used a 1-ml sample because of the low levels of chloride in beer. The 35.5 factor in the calculation is the milligrams per liter for each milliequivalent of chloride.

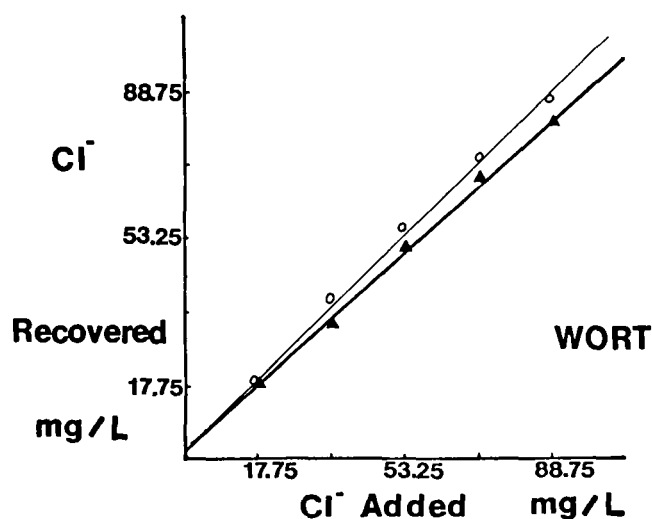


Fig. 1. Comparison of potentiometric and coulometric methods for recovery of incremental additions of chloride ion to wort.  $\blacktriangle$  = potentiometric;  $\circ$  = coulometric.

<sup>1</sup>Presented at the 47th Annual Meeting, Miami, FL, May 1981.

**TABLE I**  
Comparison of Potentiometric and Coulometric Titration Procedures  
in the Recovery of Chloride Additions to Wort

Cl <sup>-</sup> Added (mg/L)	Total Chloride Ion (Cl <sup>-</sup> )					
	Potentiometric			Coulometric		
	Calculated (mg/L)	Found (mg/L)	Recovery (%)	Calculated (mg/L)	Found (mg/L)	Recovery (%)
0	...	189.0	...	...	205.9	...
17.75	206.75	207.0	100.1	223.65	223.9	100.1
35.50	224.50	222.0	98.9	241.40	243.7	101.0
53.25	242.25	240.0	99.1	259.15	262.3	101.2
71.00	260.00	256.5	98.7	276.90	278.2	100.5
88.75	277.75	270.0	97.2	294.65	291.9	99.1

**TABLE II**  
Comparison of Potentiometric and Coulometric Titration Procedures  
in the Recovery of Chloride Additions to Beer

Cl <sup>-</sup> Added (mg/L)	Total Chloride Ion (Cl <sup>-</sup> )					
	Potentiometric			Coulometric		
	Calculated (mg/L)	Found (mg/L)	Recovery (%)	Calculated (mg/L)	Found (mg/L)	Recovery (%)
0	...	169.5	...	...	181.7	...
17.75	187.25	187.5	100.1	199.45	200.7	100.6
35.50	205.00	202.5	98.8	217.20	220.7	101.6
53.25	222.75	220.5	99.0	234.95	237.4	101.0
71.00	240.50	240.0	99.8	252.70	258.6	102.3
88.75	258.25	255.0	98.7	270.45	277.8	102.7

**TABLE III**  
Comparison of Potentiometric and Coulometric Titration Procedures  
for Chloride (Cl<sup>-</sup>) Analysis of Six Domestic Commercial Beers

Method	Domestic Beers (mg/L of Cl <sup>-</sup> ) <sup>a</sup>					
	I	II	III	IV	V	VI
Potentiometric	112.5	180.0	112.5	142.5	97.5	71.3
Coulometric	121.2	199.9	122.5	156.6	110.8	77.7

<sup>a</sup>Chloride values presented in the table are the average values for five individual analyses of each sample.

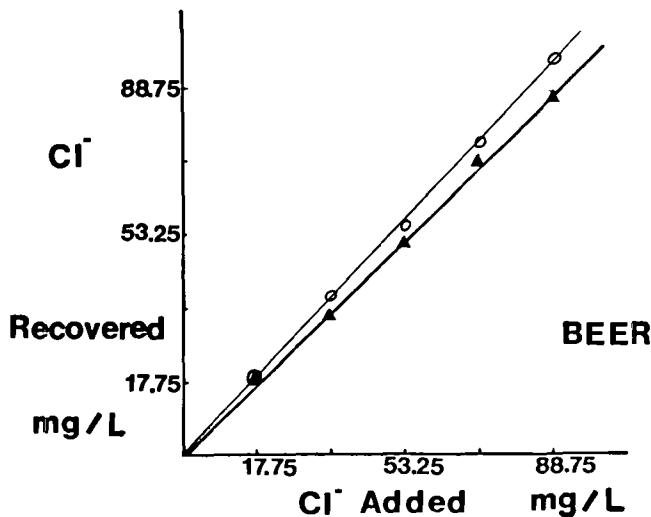


Fig. 2. Comparison of potentiometric and coulometric methods for recovery of incremental additions of chloride ion to beer. ▲ = potentiometric; ○ = coulometric.

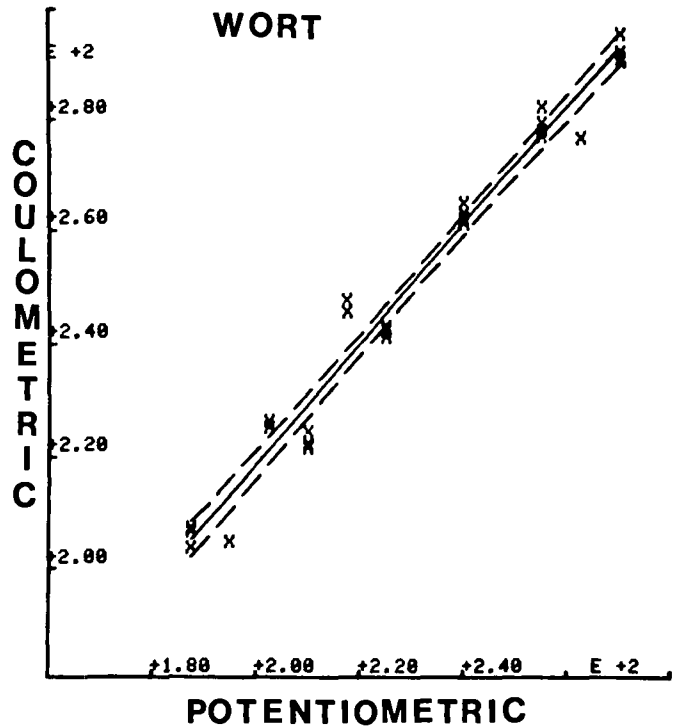


Fig. 3. Linear regression of the coulometric method on the potentiometric method for wort chloride (Cl<sup>-</sup>). Y = A + BX; A = 7.07; B = slope = 1.06. Correlation coefficient = 0.989. Standard error = 4.59. Broken lines = 95% confidence intervals.

**RESULTS AND DISCUSSION**

Comparative data pertaining to recovery of the known chloride increments are given for wort in Table I and for beer in Table II. Chloride values, also by both methods, for the series of domestic

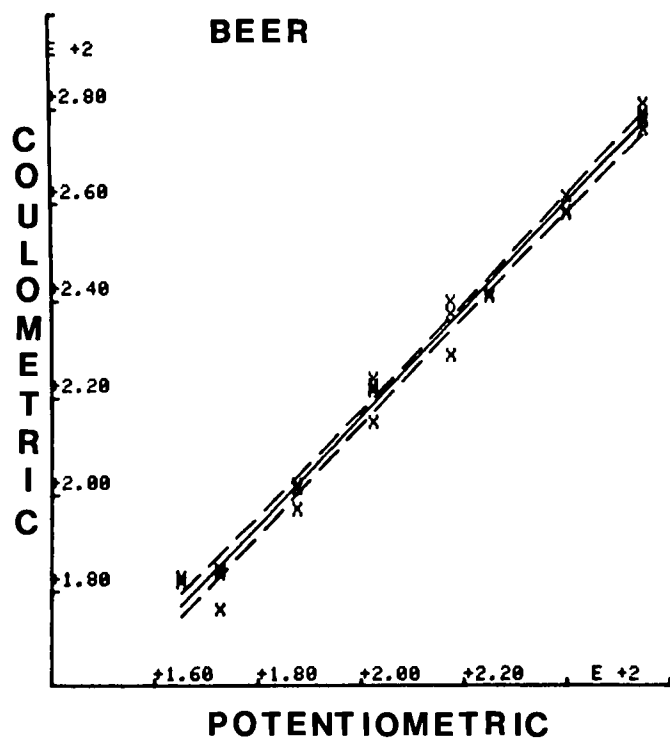


Fig. 4. Linear regression of the coulometric method on the potentiometric method for beer chloride ( $\text{Cl}^-$ ).  $Y = A + BX$ ;  $A = -5.85$ ;  $B = \text{slope} = 1.11$ . Correlation coefficient = 0.994. Standard error = 3.61. Broken lines = 95% confidence intervals.

commercial beers are given in Table III.

The data of Tables I and II show that the coulometric procedure, as applied, gave chloride results for the base wort about 8.5% higher than those found by the potentiometric procedure. They were about 7% higher with the beer used as a base for incremental additions. Comparisons of the six domestic beers (Table III), without added increments of  $\text{Cl}^-$ , similarly showed higher results for the coulometric procedure, varying from 7.7 to 13.6% higher,

with five of the six beers being in the 8–11% higher range.

Application of the recovery percentage of Tables I and II to the recovery of added chloride by the two methods is shown for wort in Fig. 1 and for beer in Fig. 2. Reflecting the trends shown in the tables, the recovery of added chloride by the coulometric procedure was slightly higher than that found for the potentiometric method. However, the correlation for the two methods was 0.989 in wort and 0.994 in beer. The correlation is better expressed in Figs. 3 and 4, which are the linear regressions of the coulometric method on the potentiometric method in wort (Fig. 3) and in beer (Fig. 4). Also, the slopes of the lines are 1.06 for wort and 1.11 for beer, indicating good agreement between the two methods.

### CONCLUSION

The automated coulometric method provides a rapid method for the determination of chloride in wort and beer and exhibits good correlation with the currently accepted ASBC potentiometric reference method. The coulometric method requires minimal setup time, preparation, and operator skill. It employs very stable reagents and requires approximately one third the time for multiple analyses.

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