Prediction and Automatic Measurement of Chill Haze[1]

M. Moll,[2] Vinh That,[2] D. Bazard,[2] L. M. Vincent,[3] and J. C. Andre[4]

ABSTRACT

The chill haze test we have developed accelerates chill haze formation by the addition of 6% v/v ethyl alcohol to degassed beer followed by rapid chilling of this solution to −8° C and measurement of the light scattered at 90°. It allows measurement of the chill haze in less than 20 min. To do this, a basic automatic apparatus was built in which a laser is the source of light and a mini-computer handles the experiment and stores the results in a memory. The coefficient of variation of the method is less than 3%, as compared with 12–15% for other methods. The values of formazin units given by this method are up to 10 times higher than those given by other methods, which indicates considerably improved sensitivity. Correlation between this new method and time colloidal stability has not yet been determined. The correlations between this method and other prediction tests for colloidal stability are significant but mediocre (r ≃ 0.7).

Key words: *Automatic measurement, Chill haze, Colloidal stability, Laser beam, Prediction*

Measurement of the chill haze of beers is important for the brewmaster because the colloidal stability of beers can be predicted and improved (1–12,15–23,26,28–36). Thus, numerous tests and types of equipment have been used to measure and/or predict the tendency of beers to form chill haze (Table I) (24). The traditional methods of prediction of the colloidal stability of beer, which indicate the true stability of beer after six months' storage, are inconvenient in taking such a long time to complete that the results are not normally known before the beer has left the brewery. This means that no treatment suggested by the results can be applied to the beer (10,12,15,20,26). For this reason, our laboratories developed an industrial alcohol-cooling test (7,8), which is currently used in quality control laboratories (25,27). However, such manual methods cannot be automated and cannot be organized to provide automatic measurement of the colloidal stability of filtered beer in a tank before packaging.

In this paper we describe a simple, rapid, and automated method for measuring chill haze, using a piece of automatic equipment[5] that we have constructed and with which measurement of the colloidal stability of a beer is possible, by means of a laser beam, within approximately 15 min.

[1] Presented at the 46th Annual Meeting, Minneapolis, May 1980.
[2] TEPRAL, 2 rue Gabriel Bour, 54250 Champigneulles, France.
[3] L.S.G.C., E.N.S.I.C., 1 rue Grandville, 54042 Nancy Cédex, France.
[4] Laboratoire de Chimie Générale, E.N.S.I.C., 1 rue Grandville, 54042 Nancy Cédex, France.

0361-0470/81/01001505/$03.00/0
©1981 American Society of Brewing Chemists, Inc.

EXPERIMENTAL

Equipment

Measuring Equipment: He-Ne Laser. The principle of the equipment is shown in Fig. 1. It is based on the simultaneous measurement of the exciting luminous flux (S_0) and the scattered flux (S_1) so that the effects of fluctuation of the intensity of the laser emission are eliminated. Because the quantity of scattered light is small, we have chosen to use a direction perpendicular to the beam. The intensity of the laser beam is measured continuously by means of a reference photocell placed perpendicular to the exciting beam and exposed to a part of the beam, which is reflected by an optical glass sheet.

[5] Patent pending.

TABLE I
Types of Equipment for Measuring Hazes

Measurement Technique	Equipment
Measurement of intensity of light scattered at 45°	Helm Clarke Zeiss-Pulfrich Lange
Measurement of intensity of light scattered at 20–26°	CBL hazemeter
Measurement of light scattered at 90°	Fisher nefluorometer Le Corvaisier Nephelometer Coleman Nephelometer Sigrist photometer Thorne and Beckley hazemeter Equipment of Jacoby Tarbox Equipment of Chapon and Chemardin Equipment of Panimolaboratorio Dognon Diffuso-absorptiometer
Measurement of back scattering	Monitek equipment

The measuring equipment comprises seven parts. A thermostated cell holder equipped with a 150-μl flow cell contains the sample to be analyzed. A constant-temperature cooling bath (Lauda RC3), set at $-8°$ C and controllable to $\pm 0.1°$ C, contains the sample carrier. The light source consists of a helium-neon laser (Spectra-Physics—138.02/236) emitting at a wavelength of 632.8 nm. At this wavelength the light flux is very stable and shows little divergence, so that the level of stray light in the equipment is considerably reduced. This light source has the advantage that interference is reduced because the substances present in beer, other than the chill-haze particles, do not absorb at this wavelength. An analytical photocell (Hamamatsu SPC 780) measures the flux of light scattered from the laser beam as it passes through the sample being analyzed; the output voltage is measured. A reference photocell (Hamamatsu SPC 780) continuously measures the intensity of the exciting laser beam. The analytical and reference photocells are placed perpendicular to the direction of the beam, give a good response at 632.8 nm, and work at low voltages that allow a reasonable life to be expected under industrial conditions. A Wood's horn is used to avoid the reflection of transmitted light. An optical glass sheet reflects part of the exciting laser beam into the reference photocell.

Data-Processing System. The simultaneous measurements of the levels of S_0 and S_1 are transferred to a microprocessor, which calculates the ratio S_1/S_0 and so eliminates effects due to fluctuations in the intensity of the laser beam. The microprocessor compares the ratio with those of a standard curve established with known suspensions of formazin (13) and registers the result directly in formazin units. Our microprocessor or microcomputer (Compucolor of Intelligent Systems Corporation) is programmable in BASIC language.

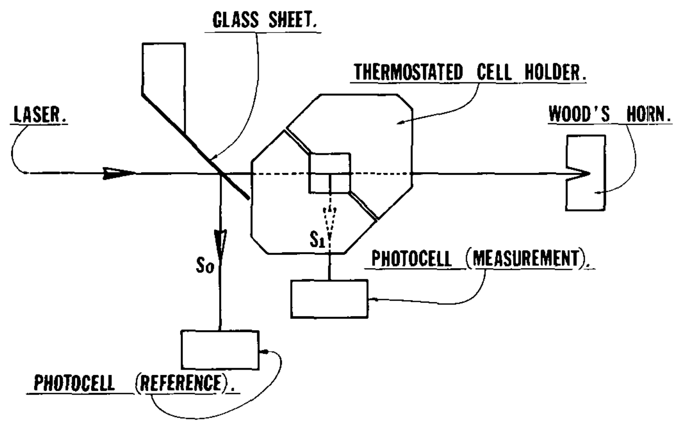

Fig. 1. Schematic diagram of equipment for measurement of chill haze. S_0 = exciting luminous flux, S_1 = scattered flux.

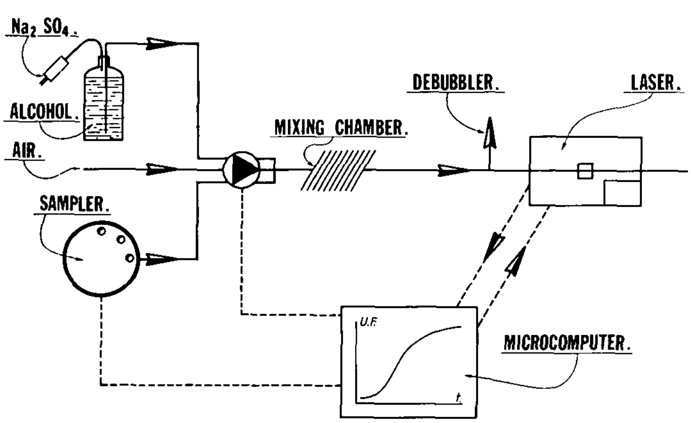

Fig. 2. Layout of equipment for preparing, introducing, and measuring chill haze.

The main program standardizes the equipment and measures up to 200 values of the haze during a period, fixed by the user, of up to 15 min. The microcomputer may then exhibit the data on its videoscreen and eventually makes a file of the data on the floppy disk on which the data are stored.

A program "Trace" allows the data to be recovered from the file and printed out as a curve showing the determined haze values as a function of time.

Other Equipment. The other units (Fig. 2) are also controlled by the microcomputer. An automatic distribution platform contains 30 conical-bottomed 9-ml tubes. The duration of sampling is adjustable, although generally in the neighborhood of 1 min, so that the product in the cell is representative of the sample to be analyzed. A peristaltic pump under programmed automatic control draws the sample from the distribution platform and alcohol from a storage flask. After these are mixed in a coil, the pump transfers the alcohol-enriched sample to the cell of the sample-carrier. The mixing coil for blending the sample with alcohol is followed by a debubbler immediately before the entry into the measuring cell. The measuring equipment is described above. A cryothermostat allows the temperature in the measuring cell to be controlled to $\pm$ 0.1° C.

Method of Operation

Calibration. The photocells measuring S_0 and S_1 are used in the same way as for the analysis of a sample. Each modification of the voltage of the photocells necessitates a new calibration; the equipment must be recalibrated before each series of analyses and the calibration must be verified regularly during each series. Suspensions of formazin having known concentrations are prepared from a standard suspension having 1,000 formazin units in 6% ethanol (v/v) (13).

A first suspension of formazin of known concentration is introduced into the chilled measuring cell from the automatic distribution platform by means of the peristaltic pump; the haze reading in formazin units of this suspension is introduced into the microcomputer, which determines, during a period of 5 min, the mean value of S_1/S_0 corresponding to this level of formazin haze. The same operation is carried out with a second suspension of formazin at known concentration.

A third solution of known concentration is injected to verify the exactness of the calibration; the microcomputer indicates the haze level in formazin units in this suspension, which should conform to the true level.

We have previously verified the linearity of the calibration curve, a typical equation for which is:

$$Y = 25.6X - 2.9$$

where Y = formazin units present and $X = S_1/S_0$.

With the above calibration data, the microcomputer gives 50.2 formazin units for a suspension known to contain 50 formazin units.

After this calibration, the equipment is ready to analyze a sample.

Preparation of Samples and Solutions. Beer, degassed before being placed in the distribution tray, is stored at room temperature and is protected from evaporation in the distribution tray by parafilm. The alcohol is protected from atmospheric humidity by a sodium sulfate drying tube. The alcohol content can be adjusted to increase or decrease the rate of formation of chill haze.

Operation. After addition of 6% (v/v) ethanol to a beer sample, the sample is injected into the measuring cell and chilled to $-8°$ C very rapidly.

A graph showing the evolution of chill haze in formazin units, based on the maximum of 200 points read in 15 min, appears on the videoscreen of the microcomputer.

The desired information, such as test number, result in formazin units after different residence times, etc., are held in memory, printed by the associated line printer, and stored on floppy disk.

After the sample tray is charged, a series of analyses can be performed without the intervention of an operator. A standard solution is injected after every 10 samples to verify the calibration of the equipment.

RESULTS AND DISCUSSION

Time Required

As a result of the very rapid chilling of the sample, the maximum value of the chill haze in the presence of alcohol is obtained in 15 min. We have found that the chill haze of a beer formed in the presence of alcohol is stable after 10 min at −8° C. We chose to print out the haze values after 5, 10, and 15 min for our first series of trials but to hold in memory only the 15-min value, which is the most reproducible one. We obtained, for instance, the values 36.6, 40.1, and 41.5 in formazin units after 5, 10, and 15 min, respectively. The time required to reach a maximum level is much longer (40–60 min) when conventional methods are used (7,10,12,15,20,26,30,36).

The speed with which the measurement can be effected allows the brewmaster to decide whether a sufficient degree of treatment has been given to the filtered beer and provides a confirmation that it may be packaged without the risk of its becoming hazy and being returned to the brewery.

Haze Level. In addition, with this new equipment, this haze level is considerably accentuated as compared to the initial test (27). For the same beer, we often find a value 10 times as high by the new method as by the old, which improves the value of the information obtained.

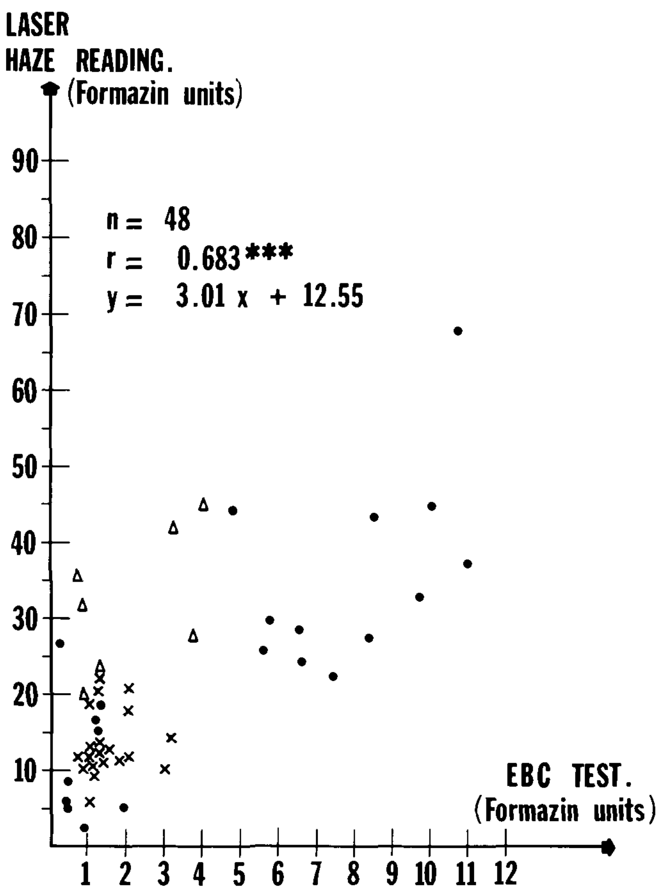

Fig. 3. Correlation between EBC haze liability test (14) and new laser technique. Δ = Beer from marketplace, • = pilot plant beer, × = beer freshly packaged in the brewery.

Reproducibility.

Table II shows that the new method gives more reliable results than do the methods currently used in our laboratories (14,27). In fact, the coefficient of variation is less than 3%, as compared with 12 and 15% with the other methods (14,27).

This better reproducibility is due to good stability and sensitivity of the measuring equipment and to the production of more haze in the new device.

Influence of the Alcohol Content

The ratio between the amounts of sample and of added alcohol must be absolutely constant for every sample; a variation of 1% in the quantity of alcohol added can result in a corresponding variation in the haze reading exceeding 25%. We chose to add 6% ethanol to the beer so as to obtain a sufficient level without unduly disturbing the natural equilibrium of the beer (7).

In addition, a very highly significant correlation ($P = 0.01$; $r = 0.978$; $y = 1.41\ x + 30.49$) was found between two methods of measurement of haze potential on 36 beers when the sole parameter varied was the concentration of alcohol.

Effect of Temperature

A variation of 1° C in the measuring cell leads to a variation in chill haze similar to that due to a difference of 1% in alcohol

TABLE II
Reproducibility of Results from Three Methods

Methods	Number of Measurements	Results (Formazin Units) Mean	Standard Deviation	Coefficient of Variation (%)
EBC[a]	29	1.1	0.17	14.75
	10	3.94	0.45	11.6
Alcohol-cooling test[b]	30	1.9	0.24	12.84
Laser				
Same bottle	10	61.5	1.64	2.67
Twenty bottles	20	12.8	0.37	2.86

[a] 12 hr at 0° C, 24 hr at 60° C, 12 hr at 0° C.
[b] −5° C, 8% ethanol.

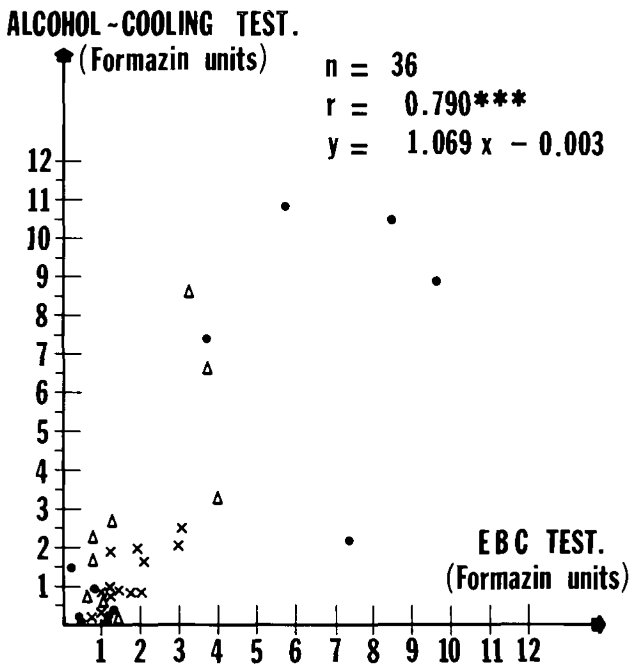

Fig. 4. Correlation between EBC test (14) and alcohol-cooling test (25). Δ = Beer from marketplace, • = pilot plant beer, × = beer freshly packaged in the brewery.

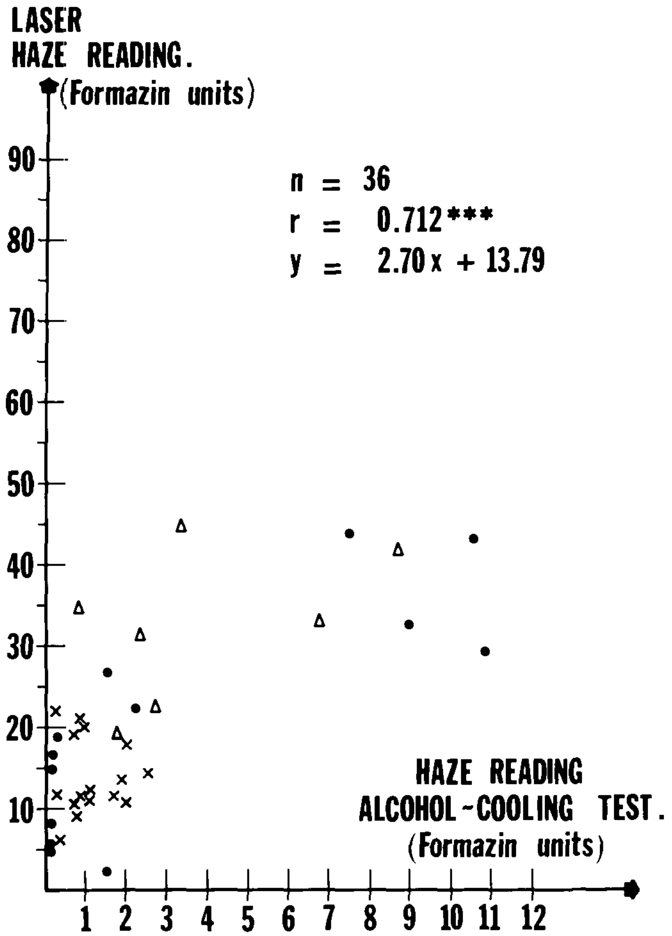

Fig. 5. Correlation between alcohol-cooling test (25) and new laser technique. Δ = Beer from marketplace, • = pilot plant beer, × = beer freshly packaged in the brewery.

concentration (7). The measurements of chill haze with 6% ethanol added are made at − 8° C to avoid the risk of freezing the beer in the measuring cell.

Relationships Between Various Prediction Tests and Colloidal Stability

A number of different beers (3–4 dozen) were used to establish the linear correlations between the different prediction tests for colloidal stability used in our laboratories. These tests compared 1) the EBC test (14) and new laser technique (Fig. 3), 2) the EBC test (14) and alcohol-cooling test (7,25) (Fig. 4), and 3) the alcohol-cooling test (7,25) and new laser technique (Fig. 5).

The correlations in the three cases are highly significant (r near 0.7), but the coefficient of determination (r^2) allows only 50–60% of the phenomenon to be explained.

Other presently undefined factors influencing the stability of beer, such as oxygen or traces of certain metal ions, may be responsible for the fact that these correlations explain only a part of the actual phenomenon. The mediocre reproducibility of the EBC test (14) and the alcohol-cooling test (27) suggest that this is part of the difficulty in obtaining correlations with a coefficient of determination above 0.9; the operating conditions of these two tests should be more strictly defined if this reproducibility is to be improved.

The conditions of formation of chill haze are different with different methods; in fact, the rate of chilling of the beer is very rapid in the method described, which may produce particles of different size from those obtained by other methods. The new method, of which the advantages and disadvantages are

TABLE III
Comparison of Different Methods of Estimation of the Chill Hazes of Beers

Method	Advantages	Disadvantages
EBC	Cheap to install Easy to operate Does not require highly qualified staff	Too long (beer has left brewery before results are known) Manual
Alcohol-Cooling Test	Fast Cheap to install Easy to operate	Manual
Laser	Able to be automatized Fast Precise Reproducible over substantial period (one month)	More expensive to install Sensitive to temperature (Cryostat must be exact to ±0.1° C)

summarized in Table III, will provide an interesting index of the probable stability, although other factors such as oxygen content will, of course, affect the true stability of the beer. A better appreciation of the different methods will be possible when the true stability of the beer after six months of storage at room temperature in the dark is known. After determining the correlation between this test and the true stability of beer, we will be able to fix a maximum value of formazin units that will alow packaging to be done with the knowledge that colloidal stability will be adequate.

CONCLUSION

This rapid and entirely automatic method of prediction of the colloidal stability of beer can be used in the quality control laboratories of breweries to evaluate the effectiveness of the treatment of the beer. The robustness of the equipment described should permit the method to be used directly at the filtered beer tank. Further, as a result of the sensitivity and good precision of the method, the laser detector should allow measurement of the haze and chill haze in less than 20 min.

LITERATURE CITED

1. American Society of Brewing Chemists. Report of Subcommittee on Turbidity in Beer. *Am. Soc. Brew. Chem., Proc. 1957,* p. 165.
2. American Society of Brewing Chemists. Report of Subcommittee on Methods for Evaluating the Chill Stability of Beer. *Am. Soc. Brew. Chem., Proc. 1958,* p. 135.
3. American Society of Brewing Chemists. Report of Subcommittee on Measurement of Chill Haze in Beer. *Am. Soc. Brew. Chem., Proc. 1959,* p. 173; *Proc. 1960,* p. 187; *Proc. 1961,* p. 133; *Proc. 1962,* p. 163.
4. Barriol, J., and Chevalier, P. *Bull. Soc. Chim. Biol.* 31:658, 1949.
5. Brandon, A. L. *Am. Soc. Brew. Chem., Proc. 1957,* p. 70.
6. Casey, O. G., and Jackson, D. S. *Am. Soc. Brew. Chem., Proc. 1964,* p. 202.
7. Chapon, L., and Chemardin, M. *Eur. Brew. Conv., Proc. Congr. 11th, Madrid, 1967,* p. 389.
8. Chapon, L., Chollot, B., and Urion, E. *Brasserie* 42:73, 1961.
9. Curtis, N. S. Page 254 in: Findley, W. P. K., ed. Modern Brewing Technology. Macmillan Press: London, 1971.
10. DeClerck, J. *Eur. Brew. Conv., Proc. Congr. 4th, Nice, 1953,* p. 161.
11. DeClerck, J. Cours de Brasserie, Vol. 2, 2nd ed. Université de Louvain, 1962, p. 586.
12. European Brewery Convention. Analytica-EBC, 2nd ed. Elsevier Pub. Co.: New York, 1963, p. 66.
13. European Brewery Convention. Analytica-EBC, 3rd ed. Schweizer Brauerei-Rundschau: Zurich, 1975, p. E79.
14. European Brewery Convention. Analytica-EBC, 3rd ed. Schweizer Brauerei Rundschau: Zurich, 1975, p. E81.
15. Ferdinandus, A. *Monatsschr. Brau.* 17(10):229, 1964.
16. Gerster, R. A. *Tech. Q. Master Brew. Assoc. Am.* 6:218, 1969.
17. Gray, P. P., and Stone, I. *Wallerstein Lab. Commun.* 2(6):24, 1939.

18. Hecht, H. *Brauwissenschaft* 8:175, 207, 235, 1955.
19. Helm, E. *Wochenschr. Brau.* 51:105, 1934.
20. Le Corvaisier, H. *Eur. Brew. Conv., Proc. Congr. 5th, Baden Baden, 1955,* p. 342.
21. Le Corvaisier, H. *Brasserie,* 12(131):164, 1957.
22. Le Corvaisier, H. *Brasserie,* 13(137):36, 1958.
23. Le Corvaisier, H. *Brasserie,* 14(149):43, 1959.
24. Moll, M. In: Pollock, J. R. A., ed. Brewing Science, Vol. 3, Academic Press: New York. In press, 1981.
25. Moll, M., Kreel, C., and Chapon, L. U.S. patent No. 3,901,068 (1975).
26. Moll, M., Vinh That, and Flayeux, R. *Wallerstein Lab. Commun.* 34(114):115, 1971.
27. Moll, M., Vinh That, and Flayeux, R. *Bios* 3:145, 1973.
28. Nummi, M., Loisa, M., Chemardin, M., and Chapon, L. *Brauwissenschaft,* 25:229, 1972.
29. Paukner, E. *Brauwelt,* 95:765, 1955.
30. Posada, J., Almenar, J., and Garcia Galindo, J. *Eur. Brew. Conv., Proc. Congr. 13th, Estoril, 1971,* p. 379.
31. Sigrist, W. *Wasser Luft Betr.* 19:3, 1975.
32. Sigrist, W. *Gas Wasser Abwasser* 791:3, 1976.
33. Simms, R. J. *Tech. Q. Master Brew. Assoc. Am.* 9:25, 1972.
34. Thorne, R. S. W., and Beckley, R. F. *J. Inst. Brew.* 64:38, 1958.
35. Thorne, R. S. W., and Nannestad, I. *J. Inst. Brew.* 65:175, 1959.
36. Wainwright, T. *Brew. Dig.* 49(5):38, 1974.

[Received May 13, 1980]