Automatic Alcohol and Real Extract Determination[1]

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ABSTRACT

The Servo-Chem automatic beer analyzer (SCABA) provides automated determinations of alcohol, specific gravity, real extract, original extract, apparent and real degree of fermentation, pH, and color. The analyzer was evaluated to determine its reliability and precision. The data obtained were compared to that obtained through the volumetric alcohol determination, ASBC method Beer-4A. The analyzer operates by oxidizing the alcohol to acetic acid, generating heat, which causes a change in the resistance of the filaments, resulting in a change in the electric current in the Wheatstone Bridge. Specific gravity was determined in situ with a Mettler Paar digital density meter. The sample data were then compared to a set of standards previously processed through the unit. All data except alcohol, specific gravity, pH, and color, were calculated by means of a series of equations using the instrument's microcomputer. After analyzing replicate beer samples, statistical analysis of the two methods indicated no difference in precision (variance). The Student's *t* test for individual samples generally indicated a difference between the mean ASBC values and the mean SCABA values for both alcohol and real extract. Twenty samples per hour could be analyzed versus 12 distillations per shift.

A great deal of progress has been made in the automation of the determination of beer alcohol, and the use of the Anton Paar digital density meter has relieved the analyst of the laborious task of determining specific gravity with a pycnometer. Recent work by the AB Pripps Bryggerier and Servo Chem, Stockholm, Sweden, has resulted in the development of an instrument utilizing the digital density meter and common physics in conjunction with computer compilation of data (4). A similar analytical technique was reported by Sartor and Sherry in 1982 (5). Their analyses indicated that the instrumental and manual methodologies were comparable.

The Servo Chem automatic beer analyzer (SCABA) unit evaluated here is capable of analyzing any type of beer at any stage of the brewing process. A complete alcohol profile is provided, i.e., alcohol w/w or w/v%, real extract, original extract, apparent extract, real degree of fermentation, apparent degree of fermentation, and specific gravity. In addition, the unit provides color and pH data. Alcohol, specific gravity, pH, and color are measured parameters, whereas the remaining parameters of the alcohol profile are calculated values. A calculation for the determination of calorie content can also be programmed into the unit. Twenty samples per hour can be processed.

Operation of the SCABA

The purposes of our investigation were to determine how closely the analyzer results compared with those of the standard ASBC distillation method (ASBC method Beer-4A) and whether the SCABA method was as precise as the distillation method. We also wanted to determine the reliability of the unit.

A 40-ml degassed sample was taken from a sample vial into a peristaltic pump. The sample was then split, with the first portion going to the densitometer, colorimeter, and pH meter. The second portion was passed over a thermostatic coil and entered the evaporation cell where the ethanol was vaporized. The ethanol vapor was then passed through a hydrophobic filter and oxidized to acetic acid at the sensor, causing a change in the resistance measured by the Wheatstone Bridge. The Wheatstone Bridge contains two catalyst coated filaments, utilizing platinum as the catalyst. Both the density reading and the alcohol determination were then used in Tabarie's (6) or Balling's formulas (2), which are stored in the computer for the determination of the alcohol profile. This data can be stored for later use or can be used immediately depending on the computer access desired. A complete operational description of the instrument has been published (4).

EXPERIMENTAL

Equipment

A SCABA unit complete with Mettler Paar DMA 40 densitometer, colorimeter, pH meter, and automatic sampling tray, was used in this study.

A Mettler Paar DMA55 densitometer was used for the determination of specific gravity according to ASBC methods (Beer-2A) (1). Additional equipment consisted of a sonic bath (20° C), used for efficiently degassing the beer, and standard laboratory equipment.

Reagents

The cleaning and conditioning fluid was supplied by Servo Chem (type GR627). Ethanol (7.5% w/w) and 1% v/v of GR627 were mixed with distilled water. The standard ethanol solution was prepared with reagent grade Pharmco ethyl alcohol, 200 proof.

Methods

It is imperative that all samples be completely degassed and, if turbid, they must be centrifuged at greater than 3,000 rpm for 5 min. The beer was carefully decanted after centrifugation and then degassed using either the shake bottle/release cap method or the ultrasound bath method. In our studies, the ultrasound probe caused excessive alcohol loss and was not incorporated into our methods.

The daily alcohol standards for calibration were prepared by qualitatively diluting 200 proof ethanol with water to cover the expected range of beer alcohol levels. In our case the ranges were from 2.9 to 3.7% and 6.7 to 7.3% w/w. The computer was programmed with a fourth degree polynomial used to determine the linearity curve after a series of ethanol mixtures was measured by the unit at 0.5% intervals from 0 to 7.3%. The daily standards were automatically linearized against this curve.

The analyzer was conditioned for 18 min using the conditioning solution. The alcohol standards followed the conditioning solution, and 40 ml samples of degassed beer followed the standards. Program selection was made with the Motorola computer, determining which method (ASBC or EBC) of analysis was desired. Changes can be made in the computer program to accommodate special types of beer, if necessary.

Control alcohol analysis was carried out according to ASBC method Beer-4A (1). Real extract determination for the control was determined volumetrically (ASBC method Beer-5A). Statistical analysis was carried out using an HP85 basic statistics cassette. The *F* ratio and Student's *t* test were computed manually (3).

RESULTS AND DISCUSSION

The analytical program was broken down into three phases. The first phase was used to compare similarities of the two methods. Numerous data were used to evaluate the correlation coefficient between the two methods and the differences in the average results. After program changes, the second phase of testing was used to

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TABLE I
Comparison of Automatic Analyzer and Distillation Method Analyses for Light Beer, Coors Beer, and Selected Specialty Beers (Phase II)[a]

Analysis and Method	Light Beer[b] Sample Average	Difference of Averages	Standard Deviation	Correlation Coefficient	Coors Beer[c] Sample Average	Differences of Averages	Standard Deviation	Correlation Coefficient	Specialty Beers[d] Sample Average	Differences of Averages	Standard Deviation	Correlation Coefficient
Before blending												
Alcohol												
Analyzer	6.69	−0.06	0.046	0.9873	5.73	0.00	0.225	0.9964				
Distillation	6.75		0.052		5.73		0.225					
Real extract												
Analyzer	3.24	−0.01	0.084	0.9565	5.37	0.00	0.504	0.9980				
Distillation	3.25		0.085		5.37		0.398					
After blending												
Alcohol												
Analyzer	3.30	0.01	0.090	0.9699	3.73	0.02	0.265	0.9969	4.17	0.03	0.440	0.9984
Distillation	3.29		0.084		3.71		0.246		4.14		0.428	
Real Extract												
Analyzer	1.55	−0.01	0.187	0.9920	3.61	−0.05	0.345	0.9966	4.24	0.02	0.500	0.9994
Distillation	1.56		0.181		3.56		0.316		4.22		0.498	

[a] Between sample data.
[b] Between blending $n = 12$, after blending $n = 22$.
[c] Before blending $n = 18$, after blending $n = 37$.
[d] After blending $n = 17$.

determine any differences between the means for alcohol and real extracting utilizing the paired two-tailed t test. For the third phase, overall precision was determined. Statistical analysis determined the average, standard deviation, correlation coefficient, and difference between methods. The paired F ratio and paired Student's t tests were used to determine if there were significant differences between the variances and means, respectively. All differences were tested at the 95% confidence level.

Phase I Analysis

Two beer types, Coors Light and Coors Premium, were analyzed during the first phase of testing. These two beer types were further split into their respective alcohol categories before blending and after blending. In all, 104 individual samples were completely analyzed by both the control ASBC procedures and the SCABA analyzer using the SCABA program 01 (primarily ASBC formulations).

The specific gravity for each method was determined by the two digital density meters, the DMA 40 and DMA 55. The specific gravity data from each instrument, when subjected to the paired t test, indicated no variability in the instruments. If specific gravity differences were found between the instruments, it was attributable to poor sample preparation, i.e., failure to centrifuge all yeast out of a fermentor or aging sample, or failure to degas the sample properly. This was not a frequent occurrence, but sample preparation was observed closely.

The phase I statistical analyses were then grouped into two areas, before blending and after blending beers. The data accumulated for each set of analyses, on a w/w% basis, included analyzer alcohol, distillation alcohol, analyzer real extract, and distillation real extract. The statistical values, average, standard deviation, difference between means, and correlation coefficient were also calculated.

All data from this phase of testing were subjected to the paired t test. In general, for the various groups analyzed, the data indicated a significant difference in mean values for each method. The analyzer unit gave alcohol readings for the various beer categories from 0.02 to 0.05% w/w alcohol higher than the ASBC method. Real extract values were 0.01 to 0.02% higher for the analyzer unit.

Phase II

In phase II of this study, the SCABA computer program 01 was adjusted by lowering the overall alcohol reading by three-hundredths of one percent because of the consistently higher reading obtained with the SCABA unit in phase I. Phase I testing was repeated using 109 routine individual alcohol samples. Table I shows the statistics for Coors Light, Coors Premium, and a select group of specialty beers. The results between sample analyses on specialty beers showed, in general, a statistical difference in the means between methods for individual samples. Table II is a summary of all beer types before and after blending, from the second phase of testing. In general, the change in the computer program in phase II led to a lesser difference between the means for the two beer groups for between-sample testing, but when the individual alcohol and real extract data were subjected to the paired Student's t test, a significant difference was detected in the means for most of the groups. Table III shows a summary of the paired t test. Coors Light after blending and Coors Premium before blending were the only alcohol analyses that showed no significant difference between the means of the two methods. In all cases, however, lowering the SCABA program by 0.03% did decrease the difference in the means between the methods.

TABLE II
Comparison of Automatic Analyzer and Distillation Method Analyses of All Beer Before and After Blending (Phase II)[a]

Analysis and Method	Sample Average	Difference of Averages	Standard Deviation	Correlation Coefficient
Before blending				
Alcohol				
Analyzer	6.11	0.02	0.509	0.9990
Distillation	6.09		0.525	
Real extract				
Analyzer	4.53	0.03	1.120	0.9998
Distillation	4.50		1.111	
After blending				
Alcohol				
Analyzer	3.70	0.01	0.414	0.9985
Distillation	3.69		0.397	
Real extract				
Analyzer	3.17	0.03	1.099	0.9998
Distillation	3.14		1.086	

[a] Between sample data. Before blending $n = 29$, after blending $n = 79$.

Phase III

This data from phase II led to the decision to run a true test for comparison of precision. The questions asked were, Do the

TABLE III
Summary of Paired *t* Test ($\alpha = 0.05$) Automatic Analyzer vs. Distillation

Beer Type	Degrees of Freedom	Critical *t* Value	Calculated *t* Value[a] Alcohol	Real Extract
Before blending				
Coors	18	2.101	1.099*	2.00*
Coors Light	12	2.179	13.95	1.47*
All beers	29	2.045	4.21	6.52
Specialty	17	2.110	5.54	6.74
After blending				
Coors	37	2.030	3.960	3.212
Coors Light	22	2.074	0.698*	1.893*
All beers	79	1.990	8.670	9.150

[a]* = No statistical difference in means between methods.

TABLE IV
Variability Analysis for Automatic Analysis vs. Distillation[a]

	Alcohol		Real Extract	
Analysis	Analyzer	Distillation	Analyzer	Distillation
$\bar{x}$	3.114	3.115	1.419	1.405
SD $(n-1)$	0.0063	0.0065	0.0047	0.0190
$s^2\ (n-1)$	0.000040	0.000042	0.000023	0.00036
–	$0.321 \leqslant 0.952 \leqslant 3.12$		$0.0638 \leqslant 2.96$	
F ratio	two-tailed		one-tailed	

[a]Determined on 14 replicate analyses, $n-1$.

methods of analysis differ in variability? and, Is the variability of SCABA less than that of distillation? A two-tailed paired *F* ratio analysis was run on 14 replicate samples for each method. One beer type was degassed and split into 28 aliquots for this analysis.

Table IV shows a summary of the *F* ratio analysis on 14 replicate samples. The *F* ratio was between the 95% confidence limits for both the percentage alcohol and real extract analyses. There was no difference in precision between the two methods of analysis for alcohol determination. For 13 degrees of freedom $(n-1)$, $F = 3.12$, while $1/F = 0.321$. As the calculated

$$F \text{ calc.} = \frac{\text{variance method A,}}{\text{variance method B}}$$

then,

$$F \text{ calc.} = 0.000040/0.000042 = 0.952.$$

The calculated *F* calc. is not larger than the *F* and is not smaller than $1/F$, therefore, the two methods do not differ in precision.

For the real extract, the *F* ratio showed that there was a significant difference in precision between the methods. The *F* ratio for the real extract analysis indicated that the variability was less for the analyzer than for the distillation real extract determination. This is shown by a one-tailed *F* ratio analysis. A paired *t* test also showed that there was no difference in the mean values for the alcohol methods, whereas there was a difference for the real extract determination.

A continual check service is conducted weekly on individual samples in the Quality Control laboratory. The SCABA alcohol and real extract averages are compared to the values obtained by the distillation method. To date, the difference in the averages has ranged from 0.00 to 0.04%, with an average difference of 0.01%.

Instrument Care, Durability, and Service

The care of the analyzer is quite easy. Cleaning with a solution of 7.5% w/w ethanol and 1% v/v of GR627 (Servo Chem) is done before and after each day's analyses and takes approximately 30 min. Wine or wine-like solutions tend to harm the sensor because of their high tannin concentrations and must not be sampled. A sensor is available for wine analyses. Samples containing free ammonia also harm the sensor. The unit should not get wet, as may occur in an open production area, and should be used by a minimum number of operators. Training is simple; it takes less than four hours to thoroughly train an operator, which includes hands-on training. The SCABA unit was operated here daily for six months with no downtime.

Summary

The phase I analysis was utilized to check the closeness of the results from the two methods for a wide variety of alcohol levels. The SCABA continually produced results 0.02–0.05% higher than the ASBC distillation method. Phase II lowered the alcohol in the SCABA alcohol program by 0.03% to align it more closely with the distillation results. Paired *t* tests indicated that there was a difference in the means of the two methods.

The third phase of testing was used to answer the questions, Do the two methods have different variability? and, Does one method vary less than the other? The two-tailed paired *F* ratio replicate sample test showed that the alcohol methods do not vary whereas the real extract methods do. The one-tailed *F* ratio test showed that the SCABA real extract had better precision than the distillation real extract.

The routine check service showed that the SCABA was reliable. The unit has replaced full-time use of the refractive index methodology in the Quality Control laboratory. SCABA units will soon be used in production to replace the labor intensive and uncertain refractive index method. The SCABA unit is capable of processing more than 100 samples per 8-hr shift and provides a complete beer distillation profile. A program is also available for basic wort gravity analysis. The SCABA unit, if installed in a protected production environment, can precisely calculate the alcohol profile and also provide phase change information for caustic or acid phase changes.

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