$$PE = \frac{0.6745\sigma}{\sqrt{N_1}} \qquad \sigma = \sqrt{\frac{\Sigma v^2}{N}}$$

where v = residual (observation minus arithmetic mean)
Σv^2 = sum of squares of individual residuals
N = total number of individual analyses used to determine the standard deviation (σ)
N_1 = number of individuals included in sample for which probable error is sought
If N_1 = N, we have the probable error of the mean of the entire series of analyses
If N_1 = 1, we have the probable error of a single observation
If N_1 = 2, we have the probable error of the mean of duplicates

The standard of reference in this case was a graph representing the analyses of aliquots of various sizes from a solution containing a known concentration of standard As_2O_3. Each point on the graph represented the mean of 10 determinations, the points being at intervals of 5 micrograms from totals of 5 to 40 micrograms.

As the conditions under which these standard solutions were analyzed are essentially the same as those just described, the standard graph is subject to the same probable error.

The probable error for the method, then, is a combination of these two effects as expressed in the equation

$$PE = \sqrt{(PE_1)^2 + (PE_2)^2}$$

where PE = probable error of method as a whole
(PE_1) = probable error of reading referred to the standard (0.0023)
(PE_2) = probable error of standard (PE for 10 observations being 0.0010)

Substituting in the formula for propagation of error, $PE = \pm 0.0025$. If, as frequently recommended, the reference is a series of single strips from the standard solution, $(PE_2) = 0.0032$ (the PE for a single observation), using this value, the error in the method would be $PE = \pm 0.0039$. (The mean of duplicates refers to single aliquots of a standard solution.)

It seemed likely that the probable error thus found is a fixed quantity for the range from 0 to 30 or 35 micrograms. A short series was run as a check. Forty aliquots of 0.010 mg. As_2O_3 each were drawn from a standard solution. The probable error of duplicates of this series was ± 0.0023 mg. This seems to indicate that the probable error of reading strips is approximately constant over this range. The relative probable error of the method ranges from about 7 per cent for aliquots containing 30 or 35 micrograms to about 20 per cent for those containing 10 micrograms, and from there down it passes rapidly to a range in which the method is only roughly quantitative and still further to one in which it has only qualitative significance.

Recovery of Arsenic

The arsenic content of forty samples of the original portions oxidized separately was determined in duplicate. The average of each pair of duplicates was treated as a unit. The mean of this series is 0.0271 mg., and the standard deviation is 0.0034. The probable error of a single observation is ± 0.0022 (with respect to the standard graph). As this is practically identical with the PE of duplicates in the other series of determinations, the operations of digestion, etc., introduce no additional errors.

Unless the manipulator gives very close attention to the process of oxidation, charring is likely to occur. Some analysts have expressed a fear that this charring may result in a loss of arsenic. To test this point, aliquots containing 20 mg. of As_2O_3 were added to each of six samples. Three of these samples were allowed to char slightly and the other three were more completely carbonized. Within the limits of experimental error of the calomel precipitation method, there were no indications of loss of arsenic from charring.

Conclusion

The order of magnitude of the error of the Gutzeit method is indicated by the data here given. Owing to the sensitiveness of this method, however, each laboratory using the method frequently should determine its own probable error.

Observation of variations in the Gutzeit strips and application of statistical methods lead to the conclusion that when applied under ordinary commercial conditions, that is, in the absence of extraordinary precautions to control physical conditions, etc., the probable error of the mean of duplicate strips in the Gutzeit method is ± 0.0039 mg. Thus, for quantities from 35 micrograms down, the error ranges from 11 to 100 per cent, when the reference is a series of single aliquots from the standard solution.

Where a graph has been prepared from a large number of aliquots from a standard solution this error may be reduced. Take sets of, say, 20 aliquots at steps of 10, 20, 30, 40 micrograms. Plot the arithmetic means of these determinations. Use this graph as the reference, or, preferably, calculate the equation of the line and prepare a table of the values of the stains of different lengths. The probable error of the method becomes ± 0.0023, which is 7 per cent to 100 per cent for the range discussed.

If the total arsenic is more than 4 mg., necessitating an aliquot of less than 0.01 to come under 40 micrograms, the calomel method should be used.

There is no loss of arsenic in the process of oxidation, etc., even when charring takes place.

Determination of Alcohol by Pycnometer[1]

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THIS method, worked out when the prohibition law went into effect and the number of samples for alcohol determinations in the laboratory of the Pittsburgh Brewing Company increased greatly, is based on the apparent uniform expansion of dilute alcohol up to about 4.5 to 5 per cent and distilled water. Hundreds of alcohol determinations support this assumption. The advantage of this method lies in the avoidance of weighings at temperatures different from the temperature in the weighing room, with its attendant disadvantages of dew on the pycnometer and the weighing pan. Another point overlooked in most descriptions is the fact that a difference in the temperature of 0.1 degree affects the result more than a difference in weight of 1 mg.

[1] Received August 20, 1929.

Apparatus

(1) A pycnometer, preferably 50-cc., straight-stemmed, with mark on the stem and without stopper.

(2) A thermometer graduated to 0.1 degree.

(3) A water bath that can hold several flasks, containing the

distillates, and the pycnometer, and which is used to keep everything at room temperature.

Procedure

Standardize the pycnometer at room temperature, then fill with the distillate at room temperature and again weigh.

Example

Temperature of water bath, 17.8° C.	
Weight of water in pycnometer, 49.8905 grams	
Weight of 100 cc. water at 20° C., according to Bureau of Standards alcohol table	99.8230
Twice the foregoing weight of water	99.7810
Difference	0.0420

Now fill the pycnometer with the alcoholic distillate. Let rest a minute or two in the water bath, when the thermometer should still read 17.8° C., and weigh. Double the weight of the distillate and add the difference, 0.0420 gram which gives the weight of the distillate at 20° C. Take the alcohol from the Bureau of Standards table. Should the weight of water in the pycnometer exceed the weight of water at standard temperature, the difference will have to be deducted instead of added.

Results are accurate to 0.01 per cent and are more reliable than those obtained in the ordinary manner, owing to the uncertainty of the temperature, which should be accurate to 0.1° C.

When dealing with higher percentages of alcohol it pays to dilute "down," so as to obtain a distillate with less than 5 per cent alcohol.

Determination of the Relative Diastatic Powers of Malt[1]

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THE Lintner value of a malt sample as reported by any laboratory depends on the particular lot of soluble starch used in the test. Hence the probability that two chemists will check each other is contingent upon the same condition, even though the same degree of carefulness and the same technic are employed in both cases.

Lintner (*3*) carefully defined the conditions of carrying out the test and preparing the soluble starch to be used. Since that time many modifications of his method have been proposed, most of which successfully shortened the rather cumbersome original procedure. And the modifications have been modified, until at the present time almost every laboratory is using a similar yet different method of determining Lintner degrees. Soluble starch according to Lintner, bearing the labels of the most reputable manufacturers, can be purchased at any supply house. It has been the writer's experience that successive lots are sometimes nonuniform, both in content of ready formed reducing sugars and in the ease to which the product lends itself to conversion by malt diastase. This condition has led many laboratories to prepare their own starch, but apparently modifications have been employed here also (*2*). The writer sent four samples of the same malt to four stations engaged more or less in referee work. The results, expressed as Lintner degrees, were 150, 188, 110, and 102. The writer's result was 138. In cases of controversy the natural tendency of the manufacturer is to accept the report of the station that found 188, and if the purchaser happens to be a client of any of the other laboratories one of two evils ensues, loss of good will or rebates.

Malt diastase can liquefy gelatinized starch as well as saccharify liquefied or soluble starch. In the Lintner test using soluble starch no measure of the first ability results. Commercially, the diastase is generally used to convert gelatinized starch and not soluble starch. Hence, if the liquefying power is appreciably impaired its saccharifying power (as measured relatively by the Lintner test) is of no avail. The liquefying power is not always in the same proportion as the saccharifying power. Lintner (*4*) proposed a method of evaluating this ability to liquefy. It is the purpose of this article to suggest a method incorporating both tests.

Diastatic activity is sensitive to pH control and the value 4.8 has been generally accepted as the optimum. Several laboratories adjust the starch solution accordingly, because it is now known that an unbuffered, so-called neutral, solution is not always neutral so far as its pH value is concerned. For the sake of uniformity we consider pH control as essential, and it should be universally employed in this test.

Procedure

Prepare a 5 per cent malt infusion by adding 250 cc. of distilled water to 12.5 grams of the finely ground sample to be tested. Carry out the digestion in a 300-cc. Erlenmeyer flask for 2 hours at room temperature. During the digestion stopper the flask and shake it continuously on a shaking machine. Meanwhile, prepare the concoction of gelatinized potato starch by weighing 2 grams of the starch into a 200-cc. volumetric flask with a rather wide neck. (The flasks used in phosphorus determinations are recommended.) The flasks previously have been tared.

Cover the starch in the flask with about 10 cc. of cold distilled water to form an emulsion-like consistency upon shaking. Pour about 175 cc. of briskly boiling distilled water into the flask and shake vigorously. Then place the flask in a boiling water bath for 15 minutes to insure complete gelatinizing. Cool to room temperature and make up the total weight of the contents to 102 grams. Temper to exactly 21° C. Filter the 2-hour malt infusion until the runnings are brilliant. Add 2 cc. of Walpole's acetate buffer to the flask containing the starch. The starch is quite viscous and a good uniform distribution is essential. Shake well. Now add 2 cc. of the filtered malt infusion and allow the reaction to proceed for exactly 30 minutes, at the end of which time arrest the reaction by adding 10 cc. of 0.1 *N* sodium hydroxide. About 10 minutes after the addition of the diastase solution the gelatinized starch will become liquefied. Until that time almost continual agitation is necessary.

In a wire rack collect a series of test tubes to which have been added 2 cc. of Fehling's solution. After the flask has been made up to its mark with distilled water and well shaken,

[1] Received August 17, 1929.