

# Determination of Alcohol Content in Beverages by Phase Titration

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In a phase titration for determination of the alcohol content of noncarbonated beverages, benzyl alcohol is added to the unknown until distinct turbidity appears, caused by the separation of a second phase. The amount of benzyl alcohol necessary to cause turbidity is a function of the ethanol content of the sample. Volume per cent of alcohol in beverages is determined by comparing the titer with a calibration curve of the titer as a function of volume

per cent of absolute alcohol in binary solutions with water. The procedure is simpler and quicker than the standard pycnometric method, and gives comparable results. Further refinement is possible for beverages containing flavoring and coloring agents which interfere slightly. Being dependent on physical rather than chemical phenomena, phase titrations are extremely general, and can be applied to many analogous problems.

**W**ater, when added to a binary solution containing a water-miscible and a water-immiscible component, causes phase separation. The resulting turbidity is more or less sharp, depending on the components and their ratio but, when distinct, it can be used to indicate a titration end point. Phase titrations have been used to analyze a large number of binary solutions of organic liquids (Bogin, 1924; Cayley and Habboush, 1961; Robertson and Jacobs, 1962; Rogers *et al.*, 1962, 1963; 1964a, b, c, 1966a, b; Spiridonova, 1946, 1947, 1949).

It is also possible to titrate binary solutions of water in a water-miscible liquid using a water-immiscible titrant. Solutions of water and pyridine have been analyzed in this laboratory using chloroform as the titrant (Rogers and Özsogomonyan, 1964a).

The same titration procedure might be of considerable practical use if applied to noncarbonated alcoholic beverages to supplement the classical methods in that field.

## THEORY

Alcoholic beverages, such as wines and whiskeys are not binary solutions but are very complex mixtures of alcohol, water, and numerous flavoring and coloring agents. Alcohol and water so predominate over the other components, however, that the authors have chosen to regard these potables as pseudo-binary solutions. The effect of small amounts of flavoring and coloring agents on phase separation appears to be small, and can be diminished by a suitable calibration procedure.

The prime factor in setting up a phase titration procedure is finding the correct titrant, because the end point is strongly dependent on the titrant for any given binary sample. The criteria for good phase titration end points have been examined in detail (Rogers and Özsogomonyan, 1963), and by applying them to the present problem, suitable titrants were selected (Table I). From these, benzyl alcohol was chosen as the best titrant by a series of preliminary experiments.

Phase titration should not be confused with Williams' field test for alcohol in beverages (Horowitz, 1960). In

phase titrations, the homogeneous unknown is titrated with a reagent immiscible in one of its components. The first phase separation serves as a turbidimetric end point. In Williams' method, an immiscible reagent is shaken with an equal volume of beverage. The volume of beverage which passes over into the immiscible phase gives a rough estimate of its alcohol content. No actual titration is involved in Williams' method, nor is there any end point.

Robertson (1962) has outlined a cloud point method of determining traces of water in ethanol. Ethanol and bicyclohexyl are made up in proportions near the critical composition. If the ethanol is pure, opacity appears suddenly in the stirred solution when the temperature drops below 23.4° C. (essentially the critical solution temperature). If 0.1% of water is present in the ethanol, opacity appears at 25.4°, if 0.2%, 27.3°, and so on. The fundamental difference between cloud point techniques and phase titration techniques is that in the former, the system passes from one to two phases at constant composition through variation in the temperature. In the latter, temperature is constant, and the second phase appears because of variations in composition. A brief discussion and summary of cloud point techniques has been given (Rogers, 1964c).

## EXPERIMENTAL

**Reagents.** Chlorine-free benzyl alcohol was obtained from Matheson Coleman & Bell. The calibration curve was constructed with reagent grade absolute ethanol from the U. S. Industrial Chemical Division, National Distillers Corp., and distilled water.

**Beverages.** Sample beverages were Widner's Lake Niagara white wine, 12.5% alcohol by volume; Gambarelli and Davitto, Fior di California burgundy scello, 13% by volume; Majorska vodka, 80 proof; Booth's gin, 90 proof; Ron Bacardi Superior, amber label, dark, 80 proof; Glen Rossie blended Scotch whisky, 80 proof; Bellows Partner's Choice blended rye whiskey, 86 proof.

**Apparatus.** Solutions were thermostatically controlled at  $25 \pm 0.25^\circ \text{C}$ ., and stirred by means of a water-driven, underwater Magjet stirrer (Will Scientific Co., Box 23, New York, N.Y.). A Tyndall lamp was used for cross-illumination.

**Procedure.** In the phase titrations, known binary solutions of absolute ethanol and water were prepared, 10-ml. aliquots were placed in 25-ml. Erlenmeyer flasks, and benzyl

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alcohol was added from a 10-ml. microburet until distinct turbidity appeared. Unknowns were titrated in the same way, and their alcohol content was determined by comparison with the calibration curve. In the case of wine, an aliquot of absolute ethanol was added to bring the sample within the optimum titration range, and the original alcohol content was back-calculated from the content of the mixture.

For comparison, the same samples were analyzed by distillation and specific gravity determination. The distillation was performed by placing a 100-ml. sample and 25 ml. of water in a 500-ml. flask fitted with a Kjeldahl spray trap and a vertical 400-mm. Liebig condenser. The sample was distilled at a uniform rate, requiring 30 to 40 minutes, until about 96 ml. of distillate had collected in a 100-ml. volumetric flask. The distillate was brought to the mark with distilled water at 20° C. The specific gravity was determined with a 10-ml. pycnometer, and its alcohol content was obtained from a conversion table (Horowitz, 1960).

Two samples were repeated using a 50-ml. pycnometer and an extended distillation time of 55 to 60 minutes as suggested in the standard procedure (Horowitz, 1960).

## RESULTS

The calibration curve for determination of the alcohol content of beverages is shown in Figure 1. Repeated titrations on 15 binary solutions of ethanol and water, with concentrations over the entire optimum titration range, were carried out. The optimum titration range has been defined as that concentration range giving titers between 0.1 and 1 times the volume of sample taken. Results showed an average deviation of 0.04% from known concentrations.

Table I shows preliminary results for other potential titrants. Titrants investigated are immiscible with water; hence, they would be applicable to binary solutions of water

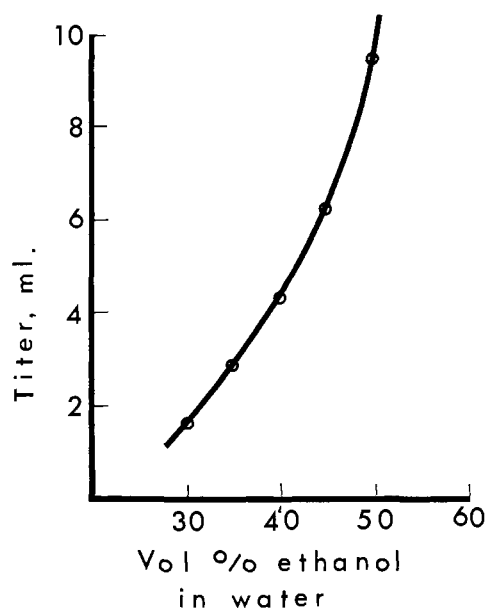


Figure 1. Volume of benzyl alcohol necessary to cause turbidity in binary solutions of ethanol and water

Table I. Preliminary Results for Several Potential Titrants

Titrant	Optimum Range, % Ethanol	Number of Titrations	Average Error, Absolute %
1-Butanol	10-30	12	0.42
2-Butanol	20-34	12	0.20
1-Pentanol	34-54	12	0.24
2-Pentanol	34-54	12	0.11
2-Octanol	50-75	12	0.06
Benzyl alcohol	30-50	12	0.11
2-Heptanone	50-70	12	0.06
Acetophenone	50-65	12	0.02
Isopentyl acetate	50-70	12	1.89
Methyl benzoate	50-65	12	2.08
Chloroform	54-80	12	0.17

and a water-miscible component such as ethanol. Titrations were carried out at room temperature, approximately 25° C. Percentage is by volume. Several are promising, but benzyl alcohol was selected. Not only does it produce good end points, but the optimum titration range is from 30 to 50% alcohol, the concentration range of most distilled alcoholic beverages. Useful titrants must also be easy to handle, have low toxicity and high stability, and be reasonably cheap. Liquids referred to in Table I might be the titrant of choice in analogous analytical problems.

Solutions referred to in Table I were not thermostatically controlled, which accounts for an average error greater than the limit of accuracy previously quoted. Moderate temperature fluctuations can double or treble the average error. Extreme temperature fluctuations must be avoided.

Table II shows the results of phase titration and analysis by the standard method for several alcoholic beverages.

## DISCUSSION

Comparison between phase titration and the standard method shows deviations between 0.11 and 0.88%. Disagreement was reduced by longer distillation time as provided for in the modified standard method, which suggests that the discrepancies may be due as much to the standard method as to the novel one.

The main error in phase titrations as performed here results from the assumption that flavoring and coloring substances do not affect the titer. The procedure could be refined by constructing the calibration curve from known solutions containing additives in such amounts and proportions as would approximate the true concentrations in the beverages to be analyzed.

Alternatively, segments of the calibration curve could be determined using samples of a given beverage to which small quantities of water or absolute ethanol have been added to vary the concentration with respect to ethanol, all other components remaining in constant concentration. Errors due to flavoring and coloring agents would tend to cancel out, providing that unknown beverages were qualitatively the same as the beverage selected as the calibration standard, and also providing that variation in the ethanol content of the unknowns was small. Both of these conditions are likely to be satisfied in practical applications.

**Table II. Specific Gravity Determination of Alcohol Content in Beverages by Phase Titration and Distillation<sup>a</sup>**

Sample	% Alcohol by Titration	End Point	% Alcohol by Distillation	Difference, %
White wine	13.74	Excellent	13.16	0.58
Red wine	13.40	Excellent	12.81	0.59
Vodka	40.46	Excellent	40.35	0.11
Gin	45.03	Very good	45.25	0.22
Gin <sup>b</sup>	45.03	Very good	45.14	0.11
Rum	40.66	Very good	39.98	0.68
Scotch	40.30	Good	39.54	0.76
Rye	42.51	Fair	43.39	0.88
Rye <sup>b</sup>	42.51	Fair	42.15	0.36

<sup>a</sup> Solutions thermostatically controlled at 25° C. Percentages by volume.

<sup>b</sup> Distillation results obtained by modified standard procedure described in text.

Relatively low deviations for phase titrations of gin and vodka may be ascribed to the small amount of flavoring in gin and its absence in vodka. The highest errors are encountered in colored wines and in whiskeys which commonly contain caramel coloring (Grossman, 1955).

#### CONCLUSIONS

Phase titrations can be carried out 20 to 30 times as rapidly as the standard method of distillation followed by density determination. One of the authors, (D.B.W.), inexperienced in both methods, found that they give results of equal accuracy. This method is submitted, therefore, to experienced beverage chemists for application to their specific problems. The authors believe that routine procedures of sufficient accuracy can be set up to make phase titrations supplement or supplant the traditional method. Some suggestions for doing so have been given. Further, phase

titrations, because they depend on the physical property of solubility and not on specific chemical properties, are very general and could find application to many analogous problems in food chemistry. In general, phase titrations have the strengths and weaknesses of other physical methods such as density determination.

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