A Spectrophotometric Method for the Determination of Water

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In 1864, Winkler (3) observed that a solution of cobaltous chloride in absolute ethanol was colored a deep blue at room temperature and that upon extreme dilution the solution retained a distinct blue color. It was also observed that the addition of water to this solution caused a color change from the blue, through violet, to pink. While this observation stimulated interest in the mechanism of the color change, the obvious application of this phenomenon received little attention. Recently, however, Ayres and Glanville (1) have reported a spectrophotometric method for the quantitative determination of water in ethanol utilizing the measurable relationship between the color of a cobaltous chloride-ethanol solution and the water concentration. Pfister and Kerley (2) have reported a similar method for the determination of water vapor in fuel gas using a cobaltous bromide-butanol solution. Both of these methods have a specific rather than a general application and an attempt is made through this investigation to outline a spectrophotometric method for the determination of water which has a broader application and which is both convenient and accurate.

General Procedure

A 1-5 gram sample of the substance containing adsorbed water is weighed into 50 ml. of absolute ethanol having a rated purity of 99.98%. The mixture is shaken vigorously for 5-10 minutes and the suspended material allowed to settle. Centrifuging may be necessary. An aliquot portion of the clear supernatant liquid is pipeted into a 50 ml., glass stoppered, volumetric flask, stock cobalt-ethanol solution is added in sufficient amount so that upon dilution the cobalt concentration will be 300 ppm., the flask is filled to the mark with absolute ethanol, and the solution mixed thoroughly. All volumetric measurements are made at 25± 0.1°C. The transmittancy of the sample solution is measured at 671mμ against absolute ethanol as the solvent and the amount of water present is determined by referring to a standard water-ethanol curve. All transmittancy measurements are made with a Beckman Model DU spectrophotometer using matched Corex cells and for the best results the cell compartment should be thermostated at 25±0.1°C.

Transmittancy Curves

Transmittancy-wavelength curves for cobalt-ethanol solutions, plotted over the wavelength range 450-750mμ, showed a minimum transmittancy at 671mμ. The concentration of cobalt does not effect the position of the minimum, however, the presence of water causes a slight shift in position toward the longer wavelengths. This is to be expected since the

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concentration of the pink aquo complex increases as the amount of water increases. Within the practical range of measurement, the minimum transmittancy of cobalt-water-ethanol solutions remains essentially constant at 671mμ.

Effect of Cobalt Concentration

The cobalt concentration determines the optimum range for the measurement of water concentration. Since cobalt-water-ethanol solutions do not obey Beer's Law, due to the formation of the aquo complex, the conditions for the measurement must be adjusted so that deviations from the law are minimized. A plot of log percent transmittancy against cobalt concentration illustrates the poor conformity to Beer's Law of cobalt-ethanol solutions even without water, however, the linear portion of the curve is in fair agreement and this suggests that the optimum cobalt concentration lies between 100 and 400 ppm.

A plot of percent transmittancy against log concentration of water for water-ethanol solutions containing first 200, then 300, and finally 400 ppm. cobalt showed that as the cobalt concentration increased, the measurable range of water concentration shifted to higher concentrations. For 300 ppm. cobalt the optimum range is from 2-10 mg. water per ml. A cobalt concentration of 300 ppm. was chosen for this determination because the ratio of the transmittancy change to change in water concentration appears to approximate that which is predicted by Beer's Law.

Effect of Time

Solutions containing 300 ppm. cobalt and varying amounts of water were measured at 671mμ and their percent transmittancy noted at five minute intervals for a period of one hour. Reproducible transmittancy readings were obtained for these solutions within ten minutes of their preparation and no noticeable change in the transmittancy was observed after one week.

Effect of Temperature

For the range 20-30°C. the transmittancy decreases approximately 1% for each degree rise in temperature. The change appears to be reversible and without effect upon the minimum transmittancy. Since the temperature has such a large effect upon the transmittancy, all solutions are thermostated at 25$\pm$ 0.1°C. before and during all transmittancy measurements.

Results of Analysis

The amount of adsorbed water in a variety of substances was determined spectrophotometrically and the values obtained checked against a Karl Fisher analysis. The results summarized in Table I are reported in milligrams of water per gram of sample.

TABLE I

Comparison of Results of Spectrophotometric and Karl Fisher Methods of Determining Water

Sample	Spectrophotometric	Karl Fisher
Sawdust	85.0	84.0
Bauxite	75.5	75.4
Cereal	2.5	2.7
Soybean mash	67.8	68.4

Summary

The change in color of cobalt-ethanol solutions from blue to pink with an increasing amount of water provides a means of quantitatively analyzing for adsorbed water if the cobalt concentration is maintained at 300 ppm., the temperature is constant to 0.1°C., and the sample is insoluble in absolute ethanol. When these conditions are observed, this spectrophotometric method may be substituted with accurate results for the widely accepted Karl Fisher method.

Literature Cited

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