

**323.** *The Determination of Small Concentrations of Alcohols.*

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An electrometric method of determining small concentrations (less than 0.05% w/v) of methyl, ethyl, *isopropyl*, *n*-propyl, and *isopentyl* alcohol is described.

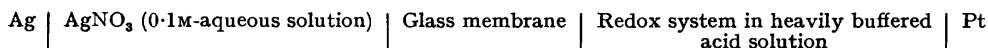
THE literature contains a variety of methods for determination of ethyl alcohol,<sup>1,2</sup> but these were not considered suitable for work in hand where a rapid method suitable for adaptation to automatic control was required; consequently an electrometric method has been developed. This involved oxidation of the alcohol by an excess of standard potassium dichromate solution, followed by electrometric back-titration of the excess with ferrous ammonium sulphate. The choice of electrodes presented some difficulty. In a preliminary investigation an irreversible electrode couple was selected, with no liquid junction.<sup>3</sup> The cell consisted of a piece of tungsten and a piece of platinum sealed separately into the flask in which the reaction was to take place. The advantage of this system is that the cell has a low resistance, and that the E.M.F. falls sharply to a value close to zero at the end-point. This arises from the fact that platinum assumes the reversible (redox) potential of the solution during the titration of dichromate with a ferrous salt, whereas the potential of tungsten is nearly unchanged. Thus at the end-point the potential of the platinum electrode falls sharply to that characteristic of the  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$  system, the overall E.M.F.

<sup>1</sup> Nicholls, "The Determination of Alcohol," *Royal Inst. Chem. Monograph*, 1947.

<sup>2</sup> Reid and Salmon, *Analyst*, 1955, **80**, 704.

<sup>3</sup> Furman, *et al.*, *J. Amer. Chem. Soc.*, 1919, **41**, 1337; 1928, **50**, 273, 277.

becoming virtually zero. While this arrangement does give a true end-point, the actual potential is far from reproducible, and the method was abandoned. Attention was then turned towards the use of the glass electrode as a reference standard in redox titrations.<sup>4,5</sup> The cell used can be written :



In this system both metal electrodes are reversible, and the reference electrode is connected to the controlling electrode through a glass membrane. The procedure normally adopted in carrying out a redox titration of this kind is to use two reversible electrodes, one as a reference standard and the other as a "reaction-controlled" electrode, the two being connected by means of a salt bridge. While this arrangement is usually satisfactory for analytical laboratory work, it is not well suited to automatic control because of the difficulties introduced by the presence of the liquid junction. It is true that the potential across the glass membrane is controlled by the pH of the redox system, but in the presence of a large amount of sulphuric acid this pH is sensibly constant and does not in any case change rapidly at the end-point, so that the potential assumed by the platinum is the sole factor governing the E.M.F. of the cell. The electrode system inside the glass membrane (Ag | AgNO<sub>3</sub>, 0.1M) was selected because the whole cell thus constituted was found to have an E.M.F. which reversed in direction at the end-point, giving a change in E.M.F. of approximately 350—400 mv for an added volume of titrant corresponding to a change of less than 0.0005% in the alcohol content of the sample. However, experiment showed that it is possible to use a normal commercial glass electrode (as used for pH determinations) in place of the above system, when the E.M.F. change is of the same order, though not showing the reversal of direction at the end-point.

The method is not absolute, and it is necessary to construct a calibration curve, by using standard solutions of alcohol and a carefully standardised technique.

#### EXPERIMENTAL

A series of ethyl alcohol-water standards, made up at concentrations 0.05, 0.036, 0.02, 0.01, 0.005, 0.002, and 0.001% w/v, was used for the construction of the calibration curves. The alcohol solution (5.0 ml.) was added to 0.025N-potassium dichromate solution (5.0 ml.), and concentrated sulphuric acid (5.0 ml.) added with stirring. The solution becomes hot, thus aiding the oxidation of the alcohol. 5 min. after addition of the sulphuric acid the solution was titrated with 0.00625N-ferrous ammonium sulphate, E.M.F. readings being taken after each addition. The oxidation is to some extent time-dependent, so that it is necessary to standardise the experimental technique and to treat both standard solutions and unknown in the same way. The curve relating volume of ferrous ammonium sulphate solution to alcohol content was very nearly linear between 0.05% and 0.01%, becoming slightly convex towards the volume axis at lower concentrations. Reproducibility was excellent, duplicate determinations agreeing consistently to within better than 0.05 ml. of ferrous ammonium sulphate solution. From about 0.05% to 0.01% this would correspond to about  $\pm 0.00015\%$  of alcohol in the original sample. The maximum displacement of any mean titration value from a smooth calibration curve was 0.1 ml., this being at an alcohol concentration of 0.005%, where such a volume corresponds to 0.0002% alcohol on the original. The method thus affords a means of determining the concentration of ethyl alcohol in aqueous solution down to at least 0.0005% (5 p.p.m.) with an estimated error of not more than  $\pm 2$  p.p.m. There does not appear to be any reference in the literature to the electrometric determination of alcohol, but Reid and Salmon<sup>2</sup> have recently described a colorimetric method, using ceric ammonium nitrate as oxidising agent. They observe that an exact timing of the oxidation period is essential, and report an accuracy of  $\pm 20$  p.p.m., their lowest concentration being 0.01% w/v. The oxidation-time factor in the method described here is only  $\pm 0.1$  ml. of ferrous ammonium sulphate/min. at 5 min., but it is obviously preferable to keep the oxidation time as constant as possible.

During the work a number of membranes was used, and whilst the absolute potential values

<sup>4</sup> Lykken and Tuemmler, *Ind. Eng. Chem. Analyt.*, 1942, **14**, 67.

<sup>5</sup> Wynd, *Ann. Missouri Bot. Garden*, 1935, **22**, 861.

were not always the same for a given alcohol concentration, the magnitude of the change at the end-point was always of the same order.

It was also found possible to determine the concentrations of methyl, *iso*- and *n*-propyl, and *isopentyl* alcohol in aqueous solutions by this method, and it is capable of further extensions.

This method has been tested on a commercial ethyl alcohol stripping column. Samples from the column had been analysed by distillation into standard dichromate solution and sulphuric acid, followed by the addition of potassium iodide and back-titration with standard thiosulphate. The agreement was within 0.005% overall (on a total of about 0.02% w/v), but the results indicated that the distillation method tended to cause a variable and indeterminate loss of alcohol.

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