NOTE.

The Elimination of Formaldehyde in the Analysis of Formaldehyde–Formic Acid Mixtures. By A. HICKLING and F. RODWELL.

No method appears to have been described for the estimation of formic acid in the presence of excess formaldehyde in solutions containing inorganic acids or alkalis. During an investigation of the electrolytic oxidation of formaldehyde it became necessary to carry out such analyses, and a suitable method has been devised by taking advantage of the almost quantitative precipitation of formaldehyde as trithioformaldehyde by the action of hydrogen sulphide in strongly acid solution (Baumann, *Ber.*, 1890, **23**, 67).

A known volume of the formaldehyde–formic acid solution, which should be free from other oxidisable compounds, is strongly acidified and treated with excess hydrogen sulphide under defined conditions (see below). The crystalline precipitate of trithioformaldehyde is filtered off, the superfluous hydrogen sulphide in the filtrate removed as copper sulphide, and the excess copper precipitated as oxide by boiling in alkaline solution. The filtrate and washings are then slightly acidified and made up to a known volume. Two equal portions of this solution are taken; in one the small amount of formaldehyde remaining is estimated by oxidation with iodine (Romijn, *Z. anal. Chem.*, 1897, **36**, 19), and in the other the combined formaldehyde + formic acid is determined by oxidation with permanganate in alkaline solution. Both results are obtained in terms of standard sodium thiosulphate solution, and the original concentration of formic acid is then readily calculated.

The following is a typical example of the application of the method. 10 C.c. of a 2M-formaldehyde solution (prepared from paraformaldehyde) containing 0·100M-formic acid were placed in a Winchester-quart bottle, and 20 c.c. of concentrated hydrochloric acid added. The bottle was then filled with hydrogen sulphide and shaken on a mechanical shaker for 3 hours, being twice refilled with gas in this time, after which it was set aside overnight. The contents were then washed through a fritted-glass filter, and 19 c.c. of approximately 10N-sodium hydroxide added to the filtrate, followed by slight excess of copper sulphate (about 3 c.c. of 0·5M-solution). The precipitated copper sulphide was then filtered off, and the filtrate boiled after being rendered alkaline with sodium hydroxide. The copper oxide was removed, and the filtrate and washings were slightly acidified with hydrochloric acid and made up to 250 c.c. The formaldehyde remaining in 100 c.c. of this solution was then estimated by adding 25 c.c. of approx. 0·1N-iodine, followed by 4N-sodium hydroxide until the solution was pale yellow; after standing for 10 minutes, the unused iodine was titrated with 0·100N-sodium thiosulphate. In general, the amount of iodine used was equivalent to 1—2 c.c. of the thiosulphate, showing that less than 1% of the formaldehyde originally present had escaped precipitation by the hydrogen sulphide. Removal of the formaldehyde to this extent seems to be essential; incomplete reaction with hydrogen sulphide appears to lead to other oxidisable substances which are soluble and are ultimately recorded as formic acid. To a second 100 c.c. portion of the solution were added 10 c.c. of 2N-sodium carbonate, followed by 50 c.c. of approximately 0·1N-potassium permanganate, and the mixture heated on a water-bath for 10 minutes. It was then cooled, excess potassium iodide added, the mixture acidified with hydrochloric acid, and the iodine titrated with 0·100N-thiosulphate. If x and y are the amounts of iodine and permanganate used, expressed in terms of the thiosulphate solution, the concentration of formic acid in the original mixture is $[0{\cdot}100(y - 2x)/8]$M. In four consecutive experiments, values of 0·101, 0·101, 0·100, and 0·101M were obtained, in close agreement with the known formic acid concentration. The presence of methyl alcohol in moderate quantity was found not to interfere markedly with the estimation; thus in an experiment in which the solution was made 0·1M with respect to methyl alcohol, the formic acid estimation was only 3% high.—CHEMICAL DEPARTMENT, UNIVERSITY COLLEGE, LEICESTER. [*Received, November 7th,* 1940.]