

A PROCESS FOR THE INDIRECT VOLUMETRIC ESTIMATION OF GLYCERIN.

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I HAVE been for some time engaged in an attempt to apply the power of glycerin in arresting the precipitation of cupric hydrate by potassium hydrate to its volumetric estimation. So far as I can discover, no process of the kind has ever yet been proposed for quantitative purposes, and an even fairly accurate method for rapidly estimating glycerin in commercial solutions of it, and in the ley from the saponification of fats, is not in existence. My experiments, although unfinished, give such good hope that the difficulties now met with may be overcome, that I think it advisable to mention the matter as it now stands. At present I can only give the process and its results, as tried on known solutions of pure glycerin, my research into the best methods of separating it from the bodies acting similarly on copper being still incomplete, but such will I hope soon follow, and then the whole will be perfect. Meantime, even a good approximate process to within a per cent. is at least a desirable advance. A great difficulty in getting reliable results, lies in obtaining for such experiments truly absolute glycerin, and although that which I used was supposed to be so, and agreed with the stated specific gravity, still, I do not pretend as yet to lay down the actual power upon copper in figures, but content myself with doing a check analysis with so-called absolute glycerin each time I standardize my solutions. It will be seen from the

subjoined figures, taken at random from a mass of analyses, and showing both the best and the worst results obtained by this method, that the process even now works fairly well:—

Glycerin taken.	Glycerin found.
1·000	·985
·905	·922
·900	·905
·500	·498
·505	·502
·504	·501
·250	·248
·251	·254
·252	·249

The first and second results are the worst I ever had, and were obtained at the commencement of the work, while the others represent the later trials; after experience and employing pure cyanide, they begin to come out very close to the truth.

The process is as follows: Take one gramme of absolute glycerin, and wash it into a long stoppered graduated tube, having a stopcock at 50 c.c. from the bottom. This tube is the same as that used in my process for the rapid estimation of olein in fats (as described and figured in *THE ANALYST*, vol. ii., page 74, and can be obtained from Messrs. Orme & Co., Barbican, E.C., who sell them as “Muter’s Olein Tubes”). Now add 50 c.c. of a strong solution of potassium hydrate (1 in 2), and then a weak solution of cupric sulphate very gradually and with constant shaking, until a fair amount of cupric hydrate is produced which remains undissolved. Make the whole up to a given bulk, and then close the tube and set it aside to settle. When perfectly clear, run off from the tap into a beaker a given volume of the deep blue liquid, and add to it the slightest possible excess of nitric acid; then pour in a definite excess of ammonium hydrate, bring the beaker under the burette charged with volumetric solution of potassium cyanide, and run in till decolourized. The number of c.c. of potassium cyanide used, after calculating to the whole bulk originally in the tube, represents one gramme of glycerin. This result has, however, to be corrected by going through the blank experiment with the same amounts of everything, *but without glycerin*, and deducting the c.c. of cyanide taken from that before found; this is necessary, because cupric hydrate is not quite insoluble in the strong alkali used, but once made and deducted, the difference gives the true value in glycerin of the cyanide solution, and that once standardized, any number of samples can be quickly analysed. I now use absolutely pure potassium cyanide, made from hydrocyanic acid, which I obtain from Germany, together with the absolute glycerin, through the agents of the firm, Messrs. Burgoyne, of Coleman Street, E.C. The source of the small error still apparent lies perhaps to some little extent in not making allowance for the space occupied by the precipitated cupric hydrate, but more especially in the inherent difficulty of working the cyanide estimation of copper to a perfectly constant point. I intend to try Bernsthen’s method of titration with sodium hydrosulphite in an atmosphere of hydrogen, with indigo as an indicator, in the hope that it may prove better, but meantime the process can claim to be as accurate as the ordinary cyanide estimation of copper will permit. I am engaged in a re-analysis of butter and other solid fats, with the view of proving, by the aid of this method, whether they are all really triglycerides or not, and hope soon to lay the results before the Society. In minute operations like these, I estimate the copper by electrolysis on platinum, which gives the required accuracy.

I may also mention that I am now trying whether better results cannot be obtained by titrating the glycerin-copper solution with pure glucose, or by using excess of glucose, igniting the precipitate with hydrogen, and weighing as metallic copper.
