

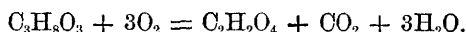
ON THE DETERMINATION OF THE GLYCERIN PRODUCED BY THE  
SAPONIFICATION OF FATTY OILS.

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THE appearance, in recent numbers of THE ANALYST, of the valuable article on "Commercial Glycerine," by Messrs. Sulman and Berry (pages 12 and 24) has recalled to the minds of chemists the fact that, until very recently, the determination of glycerin was very unsatisfactory—even Dr. Muter's copper method being only available under certain prescribed conditions.

Being interested in the determination of glycerin produced by the saponification of fatty oils, last summer I applied to Mr. William Fox, who, I knew, had made some

experiments with a process originally suggested by Mr. Wanklyn. The method depended on the oxidation of the glycerin produced by saponifying the oil by permanganate in alkaline solution, with consequent formation of oxalic acid, carbon dioxide, and water, in accordance with the equation :—



The excess of permanganate is then destroyed by a sulphite, the liquid filtered, the filtrate acidulated with acetic acid, and the oxalate precipitated by a calcium salt.

At the time of my correspondence with Mr. Fox, he was in the habit of weighing the calcium precipitate; and fully admitted that this was the weak point of the method, which, he also said, had, in his hands, never given sufficiently reliable or constant results to justify him in publishing them. This was closely followed by the publication, in the *Journal of the Society of Dyers and Colourists* for August, 1885, of the abstract of a paper by Benedikt and Zsigmondy in the *Chemiker Zeitung*, in which the volumetric determination of the oxalate was recommended; and a number of figures were given showing the proportions of glycerin yielded by the saponification of different fatty oils. On the appearance of this abstract, I called the attention of Mr. Fox to it, and expressed regret that he had not previously published his own results. He replied, acknowledging the value of the improvements introduced by Benedikt and Zsigmondy; and stating that his own results had not been satisfactory, and he was glad he had not made them public.

This being the history of the process, I was surprised to notice, in the *Chemical News* for January 8th, 1886, a note by Messrs. Fox and Wanklyn, dated December 29th, 1885, in which they claim the whole method as theirs, including the important volumetric treatment of the calcium oxalate.

The process of Benedikt and Zsigmondy has been very carefully investigated in my laboratory, during the last six months, by Mr. J. C. Belcher; and the accuracy attributed to it by Benedikt and Zsigmondy fully confirmed, so far as the determination of glycerin in aqueous liquids is concerned. When, however, the method is applied to the products of saponification of oils, a serious practical difficulty occurs. Ordinary (ethylic) alcohol yields a considerable, though variable, proportion of oxalic acid by oxidation; and, if alcoholic potash be employed for effecting saponification, it becomes practically impossible to eliminate all trace of alcohol by evaporation without incurring or risking the loss of an appreciable quantity of glycerine. To avoid this difficulty, Benedikt and Zsigmondy employ pure methyl alcohol; but I have found the article obtainable under this name in commerce to yield a very appreciable quantity of oxalic acid when evaporated with caustic alkali, and the residue oxidised with permanganate. The preparation of methyl alcohol which will stand this test has, in my hands, proved so troublesome as practically to negative its employment; and hence I have aimed at effecting saponification by aqueous alkali, and thus completely avoiding the source of error in question. Complete saponification in an aqueous liquid is, however, not easy to effect with certainty; and it is only as the outcome of numerous experiments that I have arrived at a mode of operating which appears to give

uniformly satisfactory results. This consists in treating 10 grammes of the fatty oil with a solution of 4 grammes of caustic potash in 25 c.c. of water, in a bottle, which is then closed tightly by an india-rubber stopper, firmly secured by wire, and heated in a water-oven, or in boiling water, for 6 to 10 hours, or until all oily globules have disappeared, and the contents of the bottle are perfectly homogeneous. The contents of the bottle should be thoroughly agitated from time to time. I have tried using sealed tubes heated under a pressure of ten atmospheres; but the results were not obtained more quickly, and were in no way more satisfactory, than those yielded at 100°C.\*

Saponification by water has the advantage of wholly avoiding evaporation, and possible loss of glycerin in consequence, while at the same time no reagent is employed which can by any chance yield oxalic acid on oxidation.

The saponification having been duly effected, the soap is decomposed by dilute acid in the usual way, the fatty acids separated, and one-half the aqueous liquid employed for determining the glycerin by Benedikt's process in the manner described in *THE ANALYST*, vol. x., page 206.

Instead of washing the bulky precipitate of oxides of manganese, I make up the liquid containing it to 500 c.c. (*plus* a small extra measure intended as a correction for the space occupied by the precipitate), filter, and take 400 c.c. of the filtrate for the subsequent precipitation of the oxalate as a calcium salt. I prefer, however, to treat the precipitate of calcium oxalate with dilute sulphuric acid and titrate with standard permanganate, rather than to ignite the precipitate and observe the volume of standard acid the resultant calcium carbonate will neutralise.

I have made other attempts to shorten Benedikt's process, but without material success. It appeared probable that, if the sodium sulphite employed for the excess of permanganate were used cautiously, it might be possible to titrate the filtered and acidified liquid at once with standard permanganate, and thus avoid the intermediate precipitation as calcium oxalate. Experiment has proved, however, that the use of a sulphite as a reducing agent causes the formation of a body not affected by iodine but oxidised by permanganate in acid solution, and which is probably a dithionate, and hence the results were always above the truth when the precipitation as calcium oxalate was omitted. Attempts to substitute ferrous sulphate and other reducing agents for the sodium sulphite, proved unsatisfactory.

In a future paper, I propose to deal with the quantitative results yielded by Benedikt's process. At present, I may say that they agree well in most cases with the theoretical views at present held of the constitution of fatty oils, but there are a few marked exceptions. The results leave no room for the ingenious isoglyceride theory of Wanklyn and Fox, and negative the statement of Konig, who could obtain no glycerin by saponifying oat fat, and but little from linseed oil.

\* It is a fact not generally known that the saponification of fats on a large scale by the "autoclave" process, which consists in heating the substance with water, and a base under a pressure of 8 to 12 atmospheres, is often very incomplete. Olein is more difficult to saponify than is stearine or palmitin, and hence, when the product is subjected to pressure, the solid fatty acids are almost free from neutral fats, but the "oleic acid" is apt to contain a considerable proportion of unaltered glycerides. I have found as much as 16 per cent. of unchanged fat in the oleic acid produced by a leading manufacturer.