

In these figures the approximate amount of butter fat present may be calculated. Of course it is not possible to tell how much milk powder has been used in the manufacture of the chocolate, but this is not essential. It is sufficient to establish the presence of butter fat in approximately the amount which would be expected from the quantities of milk powder usually employed in these products.

SUMMARY.

1. In order to prove a milk chocolate true to name it is necessary to establish the presence of desiccated milk. This may be done by estimation of lactose and butter fat.
2. Heating a solution of lactose to 86° decreases the polarimetric reading by an amount which may be corrected by multiplying by 1.11.
3. Sucrose and lactose may be determined in the same solution by polarizing the sucrose in the usual way and lactose at 86°, after the inversion of the sucrose.
4. These sugars may be rapidly and accurately determined in sweet and milk chocolates by the optical method described.
5. Butter fat in milk chocolate may be approximately estimated from the Reichert-Meissl number of the fat extracted therefrom.

THE ESTIMATION OF HIGHER ALCOHOLS ("FUSEL OIL") IN DISTILLED LIQUORS.

BY PHILIP SCHIDROWITZ.

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In a paper entitled "Results of Fusel Oil Determination According to the Allen-Marquardt Method as Modified by Schidrowitz" A. Lasche¹ comes to the conclusion that " * * * the results obtained by the Allen-Marquardt Method do not represent the quantities of higher alcohols or Fusel Oil contained in distilled liquors, whereas the Roesé Method results are very reliable and practically correct." This conclusion is somewhat remarkable, for Lasche finds by the Roesé Method in two series of experiments the following percentages of the Higher Alcohols added to the spirit :

Propyl Alcohol	49%	and	70%
Iso-Butyl Alcohol	66%	"	80%
Amyl Alcohol	88%	"	112%

These results Lasche calls "practically correct." These six experiments together with six similar experiments with the Allen-Marquardt Method practically constitute the whole of the work with which Lasche attempts to disprove the value of the Allen-Marquardt process.

If Lasche's experiments had been conducted on what I consider to be sound scientific principles, the results obtained by him would certainly not

¹ Lasche's Magazine, September, 1906.

have convinced me of the inefficiency of the Allen-Marquardt Method, for as compared with Lasche's *two* experiments with anylic alcohol, for instance, I have made some forty or fifty controls and very many hundreds of analyses and my results¹ have been extremely favorable. I may say that when I first began working with the method I obtained results which were by no means good, but with a little experience and attention to detail, I gradually overcame the difficulties initially experienced. I have had communications to the same effect from a number of colleagues. At first they did not like the process, but those who persevered have one and all admitted to me that they now regard it as the only process capable of giving anything like accurate and concordant results.

I have said above that even if Lasche's experiments had been conducted on sound and scientific principles, they would not have convinced me, and I have given my reason for this, but, as a matter of fact this was not the case. The higher alcohols employed by him were, to judge by the boiling points stated by Lasche, obviously very impure, and instead of employing pure alcohol as an "original spirit," he used a highly impure liquid. That is to say he adds to a liquid of unknown constitution (which he tests by the very tests which are being examined) impure higher alcohols (i. e. also substances of a comparatively unknown composition) and then applies the two processes which are to be examined. Surely he should have started with a pure, say 100 Proof, alcohol and pure higher alcohols.

There is moreover, no evidence that Lasche made any attempt to keep the liquids during the carbon tetrachloride extractions in the Allen-Marquardt process at a constant temperature, nor that he employed the special apparatus which I have recommended.

Further the whole of Lasche's results have apparently been miscalculated for he throughout adds the higher alcohols or "fusel oil" to the "original spirit" by volume, apparently *returns results by weight* and forgets to allow for the specific gravity of the added alcohol. Thus in experiment he says "To 299 cc. of original spirits added *one cc.* amyl alcohol or 0.33 per cent." Of course it is not 0.33 per cent. but 0.33×0.8137 or 0.269%, which is a very different thing.

If the correct calculation were applied, for instance to the first result with amylic alcohol, we should find approximately for

Roose Method.....	119%
Allen-Marquardt.....	76%

It is perhaps unnecessary to criticise such experiments as these any further, but I think it desirable to refer briefly to the other authorities to whom Lasche appeals. He quotes from communications received from

¹Analyst, June, 1905, and June, 1906; J. Soc. Chem. Ind., June, 1902, and June, 1905, etc., etc.

J. Koenig and from Karl Windisch, which he appears to believe bear out his contention as to the relative value of the two processes. With regard to Koenig's communication it is obvious that he is not in touch with current literature other than German on this subject, or he would scarcely say: "The Allen-Marquardt process is scarcely used any more." Again it is obvious that Dr. Koenig has little, if any personal experience of the method, or he would not refer to it as a method "which, it would seem (*angeblich*) has many drawbacks." I have the greatest respect for Dr. Koenig's work, but I am not aware that he has ever published any original matter on this subject, and I imagine that he would be the last to contend that he has any special or expert knowledge of spirit analysis or technology. I gather from Dr. Koenig's remarks that they are based not on his own personal experiments, but on such German literature on the subject as exists, namely on the work of Karl Windisch. This brings me to the second authority to whom Lasche appeals. Windisch says: "I am still of the opinion that it (*the Roese Method*) is better than the others, including that of Allen-Marquardt." Now, as I have already pointed out elsewhere¹ there is very good reason to believe that Windisch has never tried the Allen-Marquardt process at all. Towards the end of 1904² in a paper on Brandy, Windisch said:

"In this process (i.e. the Allen-Marquardt) the fusel oil is shaken out with *chloroform* * * * this process gives results which are much too low * * *" and in proof of this refers to his own work of 1889 (*Arbeit, des Kaiserl. Gesundheits a 1889, 373*).

Now the Allen-Marquardt process was not devised until 1891, and I need scarcely say that chloroform is not used in it, but that this was a feature of the original Marquardt process. It is quite clear, therefore, that Windisch's criticism in 1904 refers to the original Marquardt and not to the Allen-Marquardt process. As I pointed this out in 1905, and Windisch to the best of my knowledge, has neither replied to my remarks nor published anything further on the question, I presume that when criticising the Allen-Marquardt process he is still laboring under the delusion that it is identical with the process examined by him some 17 years ago.

So much then for the value of the "authorities" quoted by Lasche. I should have preferred so consider this subject on its own merits, but as Lasche has imported the *opinions* of others into the discussion, I propose to do the same, the difference being that those to whom I refer have not only given "opinions" but have practical experience of the process. Briefly put, if we except Lasche³, practically every worker who has given any special attention to this class of work is of the opinion that the Allen-

¹ The Analyst, June 1905.

² Z. Unters. Nahr. u. Genussm. 8. October 15, 1904.

³ I do not accept the German chemists to whom Lasche refers, for they obviously have no practical experience in the matter at issue.

Marquardt is the best process, and the great majority hold that it is the only process which actually gives anything approaching to a true result for *all classes* of spirits. The process is used¹ in the U. S. Dept. of Agriculture Laboratory. Numerous check experiments and several thousand analyses have been made by the Department, and it has been pronounced² by the Department to be the only process capable of giving concordant results. The process is used in the Laboratory of the West Australian Government and recently the West Australian Government Chemist³ has published a long paper with very numerous figures on the subject in which he comes to the conclusion that accurate results may be obtained if the precautions to which I have referred in my various papers on the subject are observed—namely, a proper shaking out temperature, prevention of loss during oxidation (either by special ground glass connections and special condenser as described by me, or by working with pressure bottles) and lastly by ignoring⁴ the methyl-orange titration.

I may point out that in the British Government Laboratory, when last some experiments on this subject were made, they discarded the Roese Method and made use of an oxidation method⁴. Further than this I may mention the following names— all of workers with practical experience in spirit analysis—of those who regard the Allen-Marquardt process as the most accurate one, namely Allen, Chattaway, Chapman, Hewitt, Tatlock, Vasey and several others. Although one or two English chemists have, at any rate until recently, considered that although the Allen-Marquardt undoubtedly gives the best results, yet the French colorimetric process may give a useful index figure, I do not know of a single chemist who has worked on the analysis of *Whiskey*, who does not regard the *Roese* process as absolutely hopeless for this purpose. And yet with certain classes of spirits the *Rose* method undoubtedly gives good results; as *Roese*, *Sell*, *Reitmayer*, *Windisch*, and more recently *Veley* have shown, it gives excellent results when pure higher alcohols are added to pure ethyl alcohol. What has been overlooked in this connection is that the *Roese* process is purely empirical, and being empirical it must necessarily have its limitations. These limitations others besides myself have found to be somewhat narrow ones; the fact that certain German and Swiss experimenters have obtained good results with rectified corn brandies, pure alcohol and so on cannot be held to neutralize the observations made by myself and others that for whiskey the process is impossible, for the simple reason that one may obtain negative results. When one is, indeed, operating with a liquor of more or less unknown composition, how can one say *what* the chloroform is extracting

¹ Bulletin No. 99. Dept. of Agriculture. Bureau of Chemistry.

² Loc. cit.

³ Mann; J. Soc. Chem. Ind. Dec. 15, 1906.

⁴ Bell, British and Foreign Spirits Committee, 1891.

from the alcoholic solution? The fact that one does occasionally obtain negative results shows that there are actually substances in some distilled liquors—and not necessarily abnormally—which cause the chloroform to pass into the dilute alcohol in part instead of vice-versa. When we consider the complicated system present during the Roese extraction, namely chloroform : ethyl alcohol : water : $(C_n H_{2n}) \times .OH$: ethereal oils : unknown substances; and that we are dealing with purely physical effects, it does not need a very great sense of discrimination to arrive at the conclusion that the Roese process can only serve in a limited capacity, particularly when we remember that a very slight physical effect is sufficient, in the Roese process, to produce a very large error in the determination. The Allen-Marquardt process, *per contra* is not empirical. What we determine is the quantity of those substances (other than aldehydes and esters, which are placed out of court by the preliminary treatment with alkali) which are capable of oxidation by means of bichromate and of forming volatile acid oxidation products. A mere trace of some unknown substance may have a very material effect in the Roese process, but in the Allen-Marquardt, the final result being obtained by a purely quantitative chemical process, the effect of this trace would be negligible. The worst then that can be said of the Allen-Marquardt process is that it gives results which are too low, the reason being that the solubility in carbon-tetrachloride of the higher alcohols (other than amyl) at the temperature and concentration of ethyl alcohol necessary to ensure an adequate separation from the latter, is different for each of the series. In a word, we know that whereas amyl alcohol is extracted quantitatively¹, it is probable that under the conditions of the process, the butyl² and propyl alcohols are not completely removed, owing to their relatively greater solubility in the alcohol : water : sodium chloride system than that of the higher alcohol of which we have most experience. This however, is a fault which applies to all the processes based on separation by means of a solvent, i. e. by extraction. It applies to the Roese process and to the Beckmann process as well as to the Allen-Marquardt process. From the considerations set out above it becomes evident

(a) that an empirical process such as the Roese can only have a limited application—i. e. that although it may give fair results for a particular type of spirit, it cannot be used indiscriminately for any type of distilled liquor.

¹ Schidrowitz and Kaye. The Analyst, June, 1905.

² The experiments in my own laboratory, by Mann, &c, conclusively prove that if the proper conditions be observed, the results for amyl alcohol are practically quantitative. It is obvious, therefore, that Lasche's figures in this regard are the result of lack of experience or of some error in working. With regard to iso-butyl alcohol, I have made a few preliminary experiments, and the results appear to indicate that there is some loss, but I doubt whether this is anything like as great as Lasche's results appear to indicate.

(b) That the Allen-Marquardt can be applied to any type of distilled liquor.

(c) That the Allen-Marquardt certainly must tend to give results that are somewhat too low, but that this is a fault applying equally to the other extraction processes—such as the Roese.

(d) That no process yet devised—or likely, in the very nature of the problem, to be devised—can give perfect results. That as between the various processes it is a choice of evils, but that the evil attendant on the use of the Allen-Marquardt process is less than in the case of the other processes.

Experience derived from experiments on a very extensive scale [*in the laboratory of the Bureau of Chemistry, Dept. of Agriculture*, (loc. cit.) *in the laboratory of the West Australian Government* (loc. cit.); in my own laboratory (loc. cit.) &c.] has shown that concordant results may be obtained by the Allen-Marquardt process and that, as far as the amyl alcohol is concerned, the results are practically quantitative. Experience has again shown that the Roese process is most unreliable and sometimes quite impossible.

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A REAGENT IN THE CHEMISTRY OF FATS.

(SECOND PAPER)¹

BY E. TWITCHELL.

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In my first paper I gave what seems to me a sufficient explanation of the special catalytic action of a series of *stearosulphonic acids* in causing the hydrolysis of glycerides of the higher fatty acids. In the presence of an excess of water a stearosulphonic acid will cause an acceleration of the hydrolysis of esters in general by virtue of its acid character, but it is a special reagent where the esters of the insoluble fatty acids are concerned as the hydrolysis of these is not accelerated by other strong acids.

A catalytic agent which would accelerate the hydrolysis of a particular class of esters in presence of an excess of water would also accelerate the esterification of their acid and alcoholic constituents in the presence of an excess of either of these two and a deficiency of water. I have found that the process of esterification of the higher fatty acids does in fact rapidly take place in the presence of a small amount of a stearosulphonic acid under conditions where, without this catalyser, the process would be so slow as not to be noticeable. The completeness of the reaction depends on the removal of the water formed and therefore the catalytic action of the stearosulphonic acids applies especially to the esterification of the higher fatty acids and alcohols which are not readily volatile at 100°, be-

¹ Read before the Cincinnati Section, Feb. 13.