THE DETERMINATION OF HIGHER ALCOHOLS IN SPIRITS.—I.

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(*Read at the Meeting, April* 5, 1905.)

Introductory.

THE present experiments were undertaken with a view to examining the relative accuracy, as far as possible, of the various processes devised for the determination of the higher alcohols in spirits, and not primarily with the object of putting forward any new method of our own. The necessity for some revision of this kind is so obvious to all chemists working in this branch of applied analytical chemistry, that an apology for its publication is scarcely necessary; but we may say, in explanation of the apparently scanty nature of the present communication, that the difficulties of the work have exceeded our anticipations. The experiments were commenced some eighteen months ago, but owing to unavoidable interruptions, and to the difficulties encountered, we are not yet in a position to publish the whole of the results obtained so far, as many of these require further confirmation. We nevertheless think it desirable to make this preliminary communication now, stating the general scope of the work, the methods of purification of the substances employed, and giving one short but, we believe, important series of results, namely, those concerning the Beckmann process, of which we, in common with many others, had hoped much, but which, unfortunately, was found to give entirely unsatisfactory results. As far as we are aware, this is the first criticism of this process that has appeared, and this fact—as it may save other workers much time and trouble—we venture to put forward in extenuation of what might otherwise be regarded as a somewhat premature paper.

Scope of Work.—We had as our object the examination of such processes only as seemed *a priori* to afford a reasonable probability of success. We selected the Beckmann nitrite process (E. Beckmann, *Zeit. Unters. Nahr. u. Genussm.*, ii., 709, and ditto, iv., 1057), the Allen-Marquardt method (ANALYST, 1891), as modified by one of us (Schidrowitz, *Journ. Soc. Chem. Ind.*, June, 1902), and finally the French colorimetric process (Girard et Cuniasse, " Manuel pratique de l'analyse des alcools et des spiritueux," Paris, 1899 : Masson). We purposely refrained from further experiments with the German official process (Röse-Stutzer-Windisch, *Arbeit des Kaiserl. Gesundheitsa.*, 1889, v., 391), inasmuch as one of us (Schidrowitz, *loc. cit.*) had shown that for one class of spirit, namely, whisky, this process was, at any rate, quite out of the question ; it gave, in fact, negative results. As it appeared likely that this might also apply to other spirits, and as one of us had had private communications from distinguished colleagues in several parts of the world confirming these observations, we did not think it worth while to devote our time to the process.

Purification of Materials ; Ethylic Alcohol.—The "pure absolute alcohol" of commerce was subjected to fractional distillation in a flask provided with a Young's "rod and disc" head until the resultant product showed no aldehyde reaction, was entirely neutral, and gave satisfactory blank tests with both the Allen-Marquardt and the colorimetric processes.

Carbon Tetrachloride.—This was first shaken with water, then boiled for several hours with chromic acid mixture, subsequently washed first with water, then with very dilute sodium bicarbonate, and finally with distilled water until neutral. The product so obtained was then further purified by distillation.

Amylic Alcohol.—Several methods of purification of the "pure" amylic alcohol of commerce (B.P., 128-132) were tried, but the following was finally adopted as being most satisfactory. The alcohol was successively shaken with dilute sulphuric acid, water, warm milk of lime, then filtered and allowed to stand overnight over solid quicklime, distilled over the latter, treated with freshly ignited sodium sulphate, distilled over the same, and finally fractionated by means of a Young's "rod and disc" apparatus. By this means we were able to obtain a product which distilled entirely within half a degree, namely, at 129·5 to 130° C.

Apparatus.—We found it a matter of very considerable difficulty to obtain an apparatus for the prolonged boiling, in the Allen-Marquardt process, of the carbon tetrachloride solution with the chromic acid mixture which was absolutely air-tight, and would permit of prolonged boiling without loss. Rubber cannot be used, and ordinary corks were found very unsatisfactory. In the same way, neither an ordinary (24-inch) Liebig nor a five-bulb condenser was capable of preventing all loss. Finally we were compelled to resort to an all-glass apparatus, consisting of a 300 c.c. Jena glass Erlenmeyer flask very carefully ground in to a 24-inch Liebig condenser, the central tube of the latter being fitted throughout its length with a Young's "rod and disc." This effectually prevents the slightest loss, and our experience is that an apparatus of this kind, if properly made, lasts for a very considerable time without cracking, and is useful for many other purposes in the laboratory, notably for the saponification of the ethers in spirits. Otherwise the apparatus used needs no special description.

A. The Beckmann Process.

This process consists substantially in a separation of the higher alcohols from the spirit (to which a certain amount of calcium chloride has been previously added) by means of carbon tetrachloride, converting the higher alcohols so isolated into their nitrites by means of nitrous acid set free by the interaction of sodium nitrite and sodium bisulphate, removing the excess of nitrous acid with sodium bicarbonate, decomposing the nitrites with sulphuric acid, and finally titrating the nitrous acid so obtained with permanganate.

Our first experiment was made (following Beckmann's instructions minutely in every detail) with a blank solution of 48·7 per cent. alcohol (by volume). The final titration in this case required some 300 c.c. $\frac{N}{30}$ permanganate, corresponding roughly to 0·8 per cent. of amylic alcohol. This was obviously an impossible result, but blank tests made with the materials (carbon tetrachloride, ice, sulphuric acid, etc.) employed failed to yield any explanation. It became therefore necessary, in the first place, to ascertain whether the fault lay in the actual process of extraction or in the treatment of the carbon tetrachloride solution with nitrous acid, etc. In order to test this point, 150 c.c. of pure carbon tetrachloride were treated with sodium bisulphate and sodium nitrite, as described by Beckmann, were then filtered, the residue being washed in accordance with the instructions, the filtrate treated with bicarbonate, water added until the excess of salt was dissolved, and the whole of the carbon tetrachloride then divided into two portions, one consisting of two-thirds of the whole, the other of the remaining third. The former was finished off according to Beckmann, and required 1·0 to 1·5 c.c. $\frac{N}{30}$ permanganate, the end, point not being sharply marked. The latter was washed with small quantities of water, filtered through a dry filter, the filter washed with a little tetrachloride, and the filtrate then treated in the manner described. In this case 0·5 c.c. permanganate was required. From these results it was quite clear that the process of nitration and subsequent removal of excess of nitrous acid, etc., is not at fault. A second blank experiment with ethylic alcohol only was made, with results practically identical with the first one. It was fairly obvious, therefore, that the extraction was the weak point, and that under the conditions employed by us a certain amount of ethylic alcohol was extracted by the tetrachloride. As we followed Beckmann's instructions minutely, we could only surmise that Beckmann in his experiments employed some peculiarly favourable alcoholic strength; for in this respect his instructions are very vague, saying as he does that the strength of the spirit to be extracted is not to be more than 50 per cent., but indicating no particular strength, as one might have expected. We therefore attempted to modify the method of extraction, finishing with the usual nitration. It struck us that in this connection the Allen-Marquardt method of extraction, which requires an approximately (according to Allen and Chattaway, *loc. cit.*) exact specific gravity of 1·1 for the solution of brine and alcohol from which the higher alcohols are extracted, might prove useful, and some experiments in this direction were therefore made; these were as follows:

1. One hundred c.c. of spirit (strength as above) were diluted with brine until they showed a specific gravity of 1·1 (by the hydrometer), and were then extracted

according to Allen. The final tetrachloride solution was then treated as in the Beckmann process. Forty c.c. permanganate were used, corresponding in terms of amylic alcohol to 1·1 grams per litre.

2. Two hundred c.c. were extracted with tetrachloride, according to the Allen method, at 15° C. exactly, and at an exact specific gravity of 1·10. After extraction the carbon tetrachloride was divided into two equal portions, the one being treated according to Beckmann, the other according to Allen.

The first required 32 c.c. permanganate (= to, roughly, 0·7 gramme per litre); the second, 2·8 c.c. $\frac{N}{10}$ baryta, of which a part was ascribable to mineral acid. If, however, in this particular case the whole of the 2·8 c.c. baryta employed were calculated in terms of amylic alcohol, it would amount to 0·24 gramme per litre, or about one-third of the blank found in the corresponding Beckmann experiment. As stated, however, a part of the Allen blank was due to mineral acid.

3. Repeated Experiment 2. In this case the Beckmann portion required 31·5 c.c. permanganate (= to, roughly, 0·7 gram per litre); the Allen portion required 2·8 c.c. $\frac{N}{10}$ baryta, of which one half was due to mineral acid. The blank in this case was, therefore, 0·12 gram per litre.

4. As Experiment 3, except that the specific gravity of the spirit extracted was purposely raised to 1·1235. In this case the Beckmann portion required 25 c.c. permanganate (= to, roughly, 0·4 gram per litre); the Allen portion, as before, an amount of baryta equivalent to, roughly, 0·1 gram per litre.

5. As before, but specific gravity of the fluid extracted was 1·0938. In this case the Beckmann portion required 35 c.c. permanganate (= to, roughly, 0·95 gram per litre); the Allen portion required (excluding the mineral acid) 3·8 c.c. baryta—that is, an amount equivalent to, roughly, 0·34 gram per litre.

The latter experiment indicates that in the Allen-Marquardt process it is desirable not to allow the specific gravity of the alcoholic brine to fall below 1·10.

From these experiments we conclude:

1. That the Beckmann process as published is unworkable.

2. That the fault lies not in the latter (nitration) part of the process, but in the actual extraction.

3. That the Allen-Marquardt process of extraction undoubtedly does ultimately leave a certain quantity of ethylic alcohol in the carbon tetrachloride extract, but that for some reason unexplained the greater part of this disappears during the oxidation with chromic acid mixture, but is not converted into acetic acid. For this curious phenomenon, which may perhaps account for the somewhat anomalous results occasionally obtained by this process, we suggest the following in explanation:

(*a*) The alcohol is split up into carbonic acid and water; or (*b*) the alcohol forms, by the action of mineral acid present or produced, an organic compound, such as ethyl chloride, for example, which does not possess acid properties.

Whether this curious action affects the higher alcohols also we are not yet in a position to say, but we hope in our second paper to be able to throw some light on this point in the course of our consideration of the Allen-Marquardt process as a whole. We are still inclined to believe that, if carefully worked, this process is still the most reliable of all those published. It appears to be very little known in some Continental quarters, particularly where the Röse process is most in favour, and in this connection we think it necessary to draw attention to some recent remarks by Karl Windisch on the subject. In a paper on Brandy contributed to the *Zeit. Unters. Nahr. u. Genussm.* (No. 8, October 15, 1904), he says (p. 488): "Ph. Schidrowitz examined twelve commercial whiskies, and determined the fusel-oil by the Allen-Marquardt method. In this process the fusel-oil is shaken out with *chloroform*,* etc. . . . This process gives *results which are much too low*" (*cf.* Karl Windisch, *Arbeit des Kaiserl. Gesundheitsa.*, 1889, v., 373). Now, this statement clearly indicates that Windisch is not familiar with the Allen modification of the Marquardt process, for one of the improvements due to Allen was the substitution of carbon tetrachloride for chloroform. It is also somewhat unfortunate for the contention of Windisch that the work to which he refers as having disproved the value of the Allen-Marquardt process was published some two years before the Allen-Marquardt process saw the light. His criticism, therefore, of the work of one of us in this respect is, to say the least, somewhat premature.

DISCUSSION.

The PRESIDENT (Mr. Bevan), in inviting discussion, said that it seemed obviously very important, not only that the alcoholic strength should be well maintained, but also that the strength of the brine solution should be kept as constant as possible. It would probably be satisfactory if a rule could be laid down for this, and he hoped that the authors might find it possible to do so in the second contribution to the knowledge of this subject which he understood they would make later on.

Mr. DIBDIN inquired whether the authors had found the temperature to vary as the strength of the solution varied, and if so, whether they had made any attempt to keep it constant.

Dr. SCHIDROWITZ said that they had all through tried to keep the temperature of the various solutions during shaking out at as nearly as possible 15° C.

Dr. J. T. HEWITT said that the authors seemed to have experimented with every available process for the determination of higher alcohols, and also to have judged the results in such a way that they knew pretty well what was to be expected from any given mode of procedure. That could not be said in every case. For instance, in the official German method—the Röse-Hertzeld method—which consisted in shaking out and merely measuring an increase in volume, it was difficult to see how any exact idea could be obtained of what it was that was being measured in any particular case. With regard to the reflux apparatus used by the authors, he had recently had the privilege of seeing this in use in Dr. Schidrowitz's laboratory, and there could be no doubt that it worked most admirably. The efficiency of condensation due to the use of the rod and disc column was surprising. It was interesting to know that a combination of the Beckmann and Allen-Marquardt methods gave good results, for both these methods seemed to be based on fairly sound principles. He should have thought that the colorimetric method would have proved more satisfactory than appeared to have been the case. Dr. Schidrowitz, however, he believed, considered that there were a good many other substances that might affect the coloration obtained with strong sulphuric acid. He (Dr. Hewitt) had been at one time inclined to think that not merely the higher alcohols, but also the higher acids, might have some influence, and he had tried removing the ethers, in addition to other

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* The italics are ours.

by-products, by prolonged boiling with caustic potash, and then determining the higher alcohols colorimetrically; and he had been surprised to find that the result was not very different from that obtained when merely the aldehydes and furfural were removed before distillation. Dr. Schidrowitz, he thought, held the view that the other substances in question were not of the nature of ethers or acids, but were of an entirely different type; and he (Dr. Hewitt) was now inclined to agree in this.

Mr. Herbert E. Burgess thought that it would be of much assistance to other workers if full details were given of the apparatus which the authors had used, and particularly of the still-head. This was different from any he had seen before. The still-head of Dr. Young was, of course, familiar, but he had never seen one with a condenser outside it. He could confirm the authors' views as to rubber connections. He had had considerable experience in distillation, and had found that, where rubber could not be used, a perfectly tight joint could be made with a wooden stopper painted round with ordinary mucilage and covered with a piece of paper, as recently described by Mr. Page in the *Chemical News*. He had been wondering whether a satisfactory estimation of the higher alcohols could be made on the lines of the method described by Dr. Thorpe for the estimation of ethers in alcoholic solution, namely, by distilling a definite quantity with a still-head of the Young-Thomas type, shaking out with petroleum ether, acetylating and saponifying.

The President said that he had rather expected some mention to be made in the paper of a new apparatus made by Messrs. Priem for the purpose of getting over the difficulty due to corks. The flask was made with a glass trough round the outside of the neck, and a mercury seal was formed by slipping over the neck of the flask another tube which dipped into mercury contained in the trough. Its only disadvantage was its liability to break, and, with a view of obviating this, he (the President) had suggested that the mercury should be retained by means of an india-rubber stopper fixed on the neck of the flask between it and the outer tube, which fitted closely over the outside of the stopper. This modification was simple to make, and had been found to work very satisfactorily.

Mr. Chapman said that owing to the difficulties which had been experienced in connection with the estimation of higher alcohols in spirituous liquids, and to the large differences which had in many instances been recorded between the results obtained by different chemists employing different methods, it was highly important that some definite information should be obtained on this subject, and to this end it was suggested to Dr. Schidrowitz and his colleague that they should direct their attention to the matter under the provisions of the Analytical Investigation Scheme which the Council of the Society had recently initiated. These gentlemen had taken the matter up very heartily, and he (Mr. Chapman) was sure that all would agree with him that the investigation could not have been placed in better hands. He thought that this was the first occasion on which the various methods for the estimation of the higher alcohols had been submitted to a critical and comparative study, and in view of the smallness of the quantities that had to be estimated, and of the very great chemical difficulties in the way, it would easily be realized how troublesome the investigation must have been. The difficulty of obtaining perfectly pure ethylic alcohol and of the preparation of solutions containing known quantities of the higher alcohols must at the outset have been very considerable. He (Mr. Chapman) had personally had experience of three methods for the estimation of the higher alcohols in spirituous liquids. The earliest was the physical method of Traube, in which an instrument known as a stalagmometer was employed. This method was only capable of being used in certain cases, and possessed a big inherent error, and he was under the impression that it was now rarely, if ever, employed. In addition to this, he had worked with Röse's process, which, so far as his experience went, was useless, and also with that of Marquardt as modified by Allen. This last-mentioned method he had used for some years, and his experience had been, on the whole, that of the authors of the present paper—viz., that it was a useful method, and one which, if properly carried out, was capable of giving good results. A great advantage which this method possessed, moreover, was that the actual oxidation products of the higher alcohols were obtained, and could be further used for purposes of examination or identification. Next to the specific gravity of the brine liquid he thought the factor which had the greatest effect on the results was the washing of the carbon tetrachloride extract. In his own experience, he had occasionally found that abnormal and impossible results were obtained by this method even when the greatest care was employed in its execution, and he would like to ask the authors whether they had ever had a similar experience. In the cases to which he referred the organic acids produced would require perhaps three or four times as much standard alkali for neutralization as they ought to, and he had usually observed at the same time that the mineral acid, instead of requiring the customary 1 c.c. or 2 c.c., would require perhaps 6 c.c., or even more, of alkali for neutralization. He would also like to ask the authors whether they had yet made any experiments with the colorimetric method which was so largely employed in France.

Dr. Schidrowitz, in reply, said that they had a number of figures which were not included in this paper, because they considered that they required amplification. The present paper was merely a preliminary communication recording the revision and control of the Beckmann method and the establishment of certain facts with regard to the Allen-Marquardt method, which would be productive of one or two slight changes in the apparatus at present in use, and so forth. Their further results would be published later on, and would include observations on the colorimetric method, with which they had made a considerable number of experiments already. With regard to the colorimetric method, although it gave fairly good results with pure amylic alcohol or iso-butylic alcohol, it obviously could not give a satisfactory result in a spirit containing a mixture of various alcohols. It was known, for instance, that, while iso-butylic alcohol gave a very strong reaction with sulphuric acid, normal propylic alcohol gave practically no reaction, and the amylic alcohol of fermentation gave a coloration which was not as strong as that given by iso-butylic alcohol. In a fermented liquid like whisky, the higher alcohols consisted, according to Bell—whose figures were the only ones available—of a mixture of about 35 per cent. of butylic alcohol, 35 per cent. of amylic alcohol, and 30 per cent. of propylic alcohol. The proportions, however, varied in every spirit, and the results obtained by acting on such a mixture with sulphuric acid and referring the colour to a standard for one particular alcohol must necessarily be misleading. They had lately made a good many parallel estimations by the Allen-Marquardt method and by the colorimetric method, and had worked out a new curve for amylic alcohol. The results were certainly interesting. He did not, however, think that they indicated higher alcohols pure and simple, but probably a variety of substances; and he agreed with

Dr. Hewitt that these probably included terpenes and substances which were not removed by saponification with potash. They had made the experiment, which Dr. Hewitt mentioned, of boiling for a long time with potash and then comparing the colorimetric results with those obtained after removing merely the aldehydes and furfural, and they had found a difference, but scarcely a radical one. The idea of putting the disc and rod column inside the condenser was their own. He thought that Dr. Thorpe's process for estimating esters would not be suitable in this case. It was only intended to apply to spirits or liquids containing relatively much larger quantities of those bodies. A process on the same lines was used for liqueurs, but they had tried it with whisky and brandy, and had found it impracticable because the quantities were so small. With regard to cork, certain substances were extracted from it by carbon tetrachloride and ether—a fatal objection to its use when the constituents to be estimated were so very minute in quantity. Ground-glass connections seemed by far the simplest, and, if properly made, seldom cracked. They had had flasks with such connections in constant use for over a year.

The PRESIDENT inquired what was used to make the joint tight.

Dr. SCHIDROWITZ said that in the Allen-Marquardt method they used sulphuric acid, but, as a matter of fact, a well-ground connection did not need anything at all. Continuing, he said that they had found that abnormal results such as Mr. Chapman mentioned were occasionally obtained, the mineral acid in the blank determination being in such cases also too high, but that in the course of a very large number of determinations recently made they had not had trouble in this direction. They could not account for this. The washing of the carbon tetrachloride solution was always carried out in the same way, and he thought it must be due to some other cause—possibly to decomposition. The mercury seal, which the President had mentioned, was originally due to Dr. Wiley, of Washington, who, however, used a differently-shaped flask, which, though suitable for fat extraction, did not readily permit of the residue being removed from the flask for quantitative purposes. They had not found them liable to crack.

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