XXX.—*The Estimation of Ethyl Alcohol in Essences and Medicinal Preparations.*

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THE estimation of ordinary alcohol in simple mixtures of alcohol and water offers no experimental difficulties. A determination of specific gravity at the standard temperature, and a reference to a table of densities, at once gives the percentage amount of spirit present.

In estimating the amount of spirit in medicinal preparations, such as tinctures of aconite, arnica, belladonna, capsicum, and calumba, these must first be distilled, as the extractive matters present would "obscure" the true percentage of alcohol as shown by the relative density.

On account of the high vapour pressure of ethyl alcohol and its avidity for water, the distillation of a strong spirituous liquid into its own volume so as to obtain an accurate determination of the amount of alcohol present in the liquid becomes practically impossible with the apparatus and the methods of distillation commonly used. It is practicable to distil a strong spirituous liquid into twice its own volume with the requisite degree of accuracy, but distillation into four times the initial volume is perfectly easy, and the results are uniformly accurate to within the degree of accuracy permitted by the spirit tables used, that is to say, if 100 cb.c. of 25 per cent. alcohol are distilled, and the volume of the distillate made up to 100 cb.c., the resulting density will be found not to differ more than 0.00001 from the original density.

The methods above indicated are obviously only applicable to preparations yielding distillates free from essential oils and other volatile substances. Hence such substances must be removed before the spirit can be estimated with any approach to accuracy. Included in this category are ether, chloroform, benzaldehyde, camphor, santal oil, castor oil, ethyl and amyl acetates and butyrates, and the essential oils of lemon, rosemary, juniper, celery, cloves and peppermint.

In such cases the method of treatment in use in the Government Laboratory and which has been found to be of very general applicability is as follows :

25 cb.c. of the sample, measured at 60° F. (15.5° C.), are mixed with water in a separator to a bulk of from 100 to 150 cb.c., and common salt is added in sufficient quantity to saturate the liquid. The mixture is now shaken vigorously for 5 minutes with from 50 to 80

cb.c. of light petroleum, boiling below 60° C., and after standing for about half an hour, the lower layer is drawn off into another separator, extracted if necessary a second time with petroleum and then drawn off into a distillation flask. Meanwhile the petroleum layers are washed successively with 25 cb.c. of saturated common salt solution, and the washings added to the main bulk, which is neutralised if necessary, and then distilled and the distillate made up to 100 cb.c.

That the whole of the alcohol which may be present can be recovered by this treatment has been proved by direct experiment with known volumes of spirit of known strength.

It has been found that the alcohol in 25 cb.c. of strong spirit when diluted with water even to the extent of 500 cb.c. and the solution saturated with common salt, can be entirely recovered in the first 100 cb.c. of the distillate.

The results thus obtained require a small correction from the circumstance that, as the alcohol present is distilled into four times its initial volume, the errors of the spirit tables are necessarily quadrupled.

The magnitude of the error can, however, be readily ascertained, once for all, by diluting quantities of 25 cb.c. of spirit of known but of varying strength to 100 cb.c. and determining the sp. gr. of the diluted spirit. There is practically no error due to distillation. The same results are obtained by simple dilution as by distillation into quadruple bulk.

A series of concurrent observations were made in the case of alcoholic mixtures of strengths varying between 160 and 88 per cent. proof spirit, and from the results of these the mean error of the tables at below 40 per cent. proof (say 0.972 sp. gr.), which is the particular section of the tables which is mainly used, may be set down as + 0.2 per cent. of proof spirit, and hence the observed determinations of spirit require a subtractive correction of 0.8 per cent.

The method, as described, is applicable to preparations containing chloroform, ether, benzaldehyde and compound ethers. In the greater number of other cases, for example, essences of lemon, juniper, peppermint and santal oil preparations, it will be found that a single extraction with petroleum is sufficient.

The same method may be applied to distillates which unexpectedly contain oily matter, or which have been obtained intermediately in order to facilitate subsequent extraction, as in the case of *Liq. Picis Carb. B. P.*

In the case of all preparations containing camphor, 25 cb.c. of normal sulphuric acid solution are used instead of common salt, and a single extraction with petroleum is made. Before distilling, it is desirable

to neutralise the sulphuric acid with caustic soda, and if by any chance the volume of the liquid becomes inconveniently large, some common salt is also added. But in preparations containing ammonia this is inadmissible, and the liquid to be distilled must be slightly acid.

This process has been in use in the Government Laboratory for some time past, and many thousands of samples containing a great variety of essential oils and other substances, have been tested by means of it.

The following results obtained on preparations actually made in the laboratory and containing known quantities of ethyl alcohol, are adduced as evidence of the accuracy and general applicability of the method:

Rectified spirit containing	Alcoholic strength of preparation, calculated.		Alcoholic strength found.	
	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.
	cb.c.		cb.c.	
20 per cent. ethyl acetate	72·8	127·6	72·6	127·3
20 „ amyl acetate	72·4	127·0	72·5	127·1
30 „ ethyl ether, B. P.	63·5	111·4	63·4	111·1
30 „ chloroform, B. P.	63·5	111·4	63·4	111·2
10 „ camphor, B. P.	81·7	143·3	81·4	142·7
10 „ lemon oil	81·9	143·5	82·1	143·9
10 „ rosemary oil, B. P.	81·6	143·0	81·4	142·7
10 „ benzaldehyde	81·9	143·6	81·4	142·7
10 „ santal oil	81·2	142·3	81·0	142·0
10 „ peppermint oil, B. P.	82·0	143·8	81·6	143·0
5 „ juniper oil, B. P.	86·4	151·5	86·3	151·2
20 „ fusel oil	72·8	127·6	72·2	126·5
<i>Lia. saponis</i> , B. P.	62·5	109·5	62·7	109·9
<i>Tr. chlor. and morph. co.</i> , B. P.	55·5	97·3	55·5	97·2
<i>Liq. sinapis</i> , B. P.	66·8	117·1	66·9	117·3
<i>Liq. picis. carb.</i> , B. P.	82·4	144·4	82·2	144·0

As evidence of the degree of variation which may be expected to occur between the results of different operators we append the following results:

Results of Different Operators.

	A.		B.		C.		D.		Alcoholic strength of preparation, calculated.	
	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.	Volume of alcohol in 100 cb.c.	Percentage of proof spirit.
Spirits of chloroform (33 per cent.)	cb.c. 60·0	105·1	cb.c. 60·1	105·4	cb.c. 59·9	105·0	cb.c. —	—	cb.c. 60·1	105·3
Spirits of ether (33 per cent.)	59·9	105·0	60·1	105·3	59·8	104·9	60·0	105·2	60·1	105·3
Spirits of camphor (10 per cent.)	81·1	142·2	81·0	142·0	81·2	142·3	—	—	81·4	142·7
<i>Liq. saponis</i>	62·9	110·2	62·8	110·1	63·2	110·7	63·4	111·0	63·4	111·1
<i>Tr. chlor. and morph. Co.</i>	49·9	87·4	49·5	86·8	49·8	87·2	—	—	49·8	87·3
Essence of lemon	73·2	128·3	73·2	128·4	73·4	128·7	—	—	73·2	128·2
Ethyl acetate in alcohol (20 per cent.)	72·7	127·5	73·5	128·9	72·7	127·5	—	—	73·1	128·1
Fusel oil in alcohol (20 per cent.)	72·2	126·6	71·9	126·0	72·5	127·0	—	—	72·8	127·7

GOVERNMENT LABORATORY,
LONDON.

VOL. LXXXIII.

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