

THE EFFECT OF THE TARTARIC ACID CONTENT OF  
WINE ON THE COMPOSITION OF DISTILLATES.

J.R. Walters,  
Roseworthy Agricultural College.

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## INTRODUCTION.

In the production of brandy the base wine, together with the methods of distillation employed, is responsible for the composition and hence the quality of the distillates.

In the past the effect of distillation procedure has been studied and it has been proved that the composition of brandy can be greatly altered with varying technique. However, little is known of the effect of the composition of the base wine on the distillate. To study this exhaustively would be beyond the scope of this paper, but the following experiment has been designed to find the effect of tartaric acid concentration. This acid is the characteristic acid of the grape and is predominant in over-ripeness, being present as bitartrate and tartrate salts which are precipitated to a considerable extent during fermentation. It is a usual addition in the acid form during vintage operations and, when this is practiced it represents a considerable portion of the acid in the finished wine.

In literature dealing with the production of cognac, the fact that wines are always of high acidity is stressed. In under-ripe grapes malic acid would be predominant but this would not be so under Australian conditions where grapes for distillation are usually picked at extreme ripeness.

## LITERATURE REVIEW.

Angove (1) found in his work that there was a marked difference in spirits distilled from wine with and without lees respectively. He found an increase in acids and esters and a decrease in aldehyde on distillation in the

presence of lees, and states that the decrease in aldehydes may be credited to the large concentration of potassium bitartrate in the lees.

Valaer (3) states that wines for cognac in France are characterised by a high acidity. It has been proved, however, that brandies can be distilled from average Australian material which very closely resemble cognac in analysis if certain methods of distillation are used, Graham (5) and Angove (1).

Renee and Jean Lafon (6) state that tartrates in solution with wine distilled on lees react with alcohols giving esters. Valaer (3) states that in the production of cognac, distillation is carried out on lees, and immediately following vintage. Under these conditions in Australia the tartrate content of the wine would be at a maximum level.

Aldehyde is an undesirable impurity in brandy in large amounts and its elimination or production in smaller quantities is important in the distillation of high quality pot brandies.

Esters are said to be produced to a limited extent during distillation. They are the important flavouring constituents of brandy and their formation appears to be related to acid content. The bearing of tartaric acid content on the amounts of these constituents present in the distillates is the object of this experiment, the theory being that a higher ester and low aldehyde content would result.

EXPERIMENTAL.

Apparatus and materials:-

1. Four six gallon glass jars.
2. Approximately 24 gallons of blended Grenache and Pedro juice, Beaune 12.2 pH 3.52
3. The still: A 2 gallon, copper pot still with open column, connected to a condenser with a constant head water supply and heated by an electric hot plate.
4. Specific gravity hydrometers covering range 50 O.P. to 100 U.P.

Methods of Analysis.

- Alcohol: - Specific gravity % by volume.
- Acids: - Direct titration (phenolphthalein) expressed as parts of acetic acid per 100,000 parts of absolute alcohol.
- Esters: - A.O.A.C. (2), as parts ethyl acetate per 100,000 parts A.A.
- Aldehydes: - P. Jaulines and Espezel (4), parts acetaldehyde per 100,000 parts A.A.
- pH: - Glass electrode potentiometer.
- Sugar: - R.A.C. notes gm/litre.
- Lactic Acid - Moslinger method, R.A.C. notes gm/litre.
- Tartaric Acid: - Pasteur-Raboul, R.A.C. notes gm/litre.
- Total Acid: - Direct titration with phenolphthalein as gm/ tartaric acid per litre.
- Volatile Acid: - Sellier tube and titration as gm. acetic acid per litre.

Procedure.

In order to obtain a wide variation in tartaric acid content in the base wine, pH was adjusted to 3.8 by addition

of calcium carbonate and to 2.8 with tartaric acid. In each case the required additions were determined by trial and mixed with the unfermented grape juice. Tartaric acid was added at the rate of 6 gms/litre and calcium carbonate at the rate of 2 gms/litre.

Each of these pH levels was obtained in duplicate and fermented and distilled under conditions which were standardised as far as possible. The juices were seeded with a pure culture of 'champagne yeast' and fermented out in glass jars for a period of four weeks during which they were fitted with hydraulic bungs.

In the tables the analyses of wines of low pH and the distillates from them are shown under "A" and those of high pH under "B" duplicate results being shown throughout.

The juice used in the experiment was comparatively clear and the quantity of lees deposited not great. This deposit was not included in the distillation charges.

All of the wine was distilled to low wines before final distillation to brandy and the three low wine distillates from each lot were bulked as shown in the plan.

Analysis of Wines.

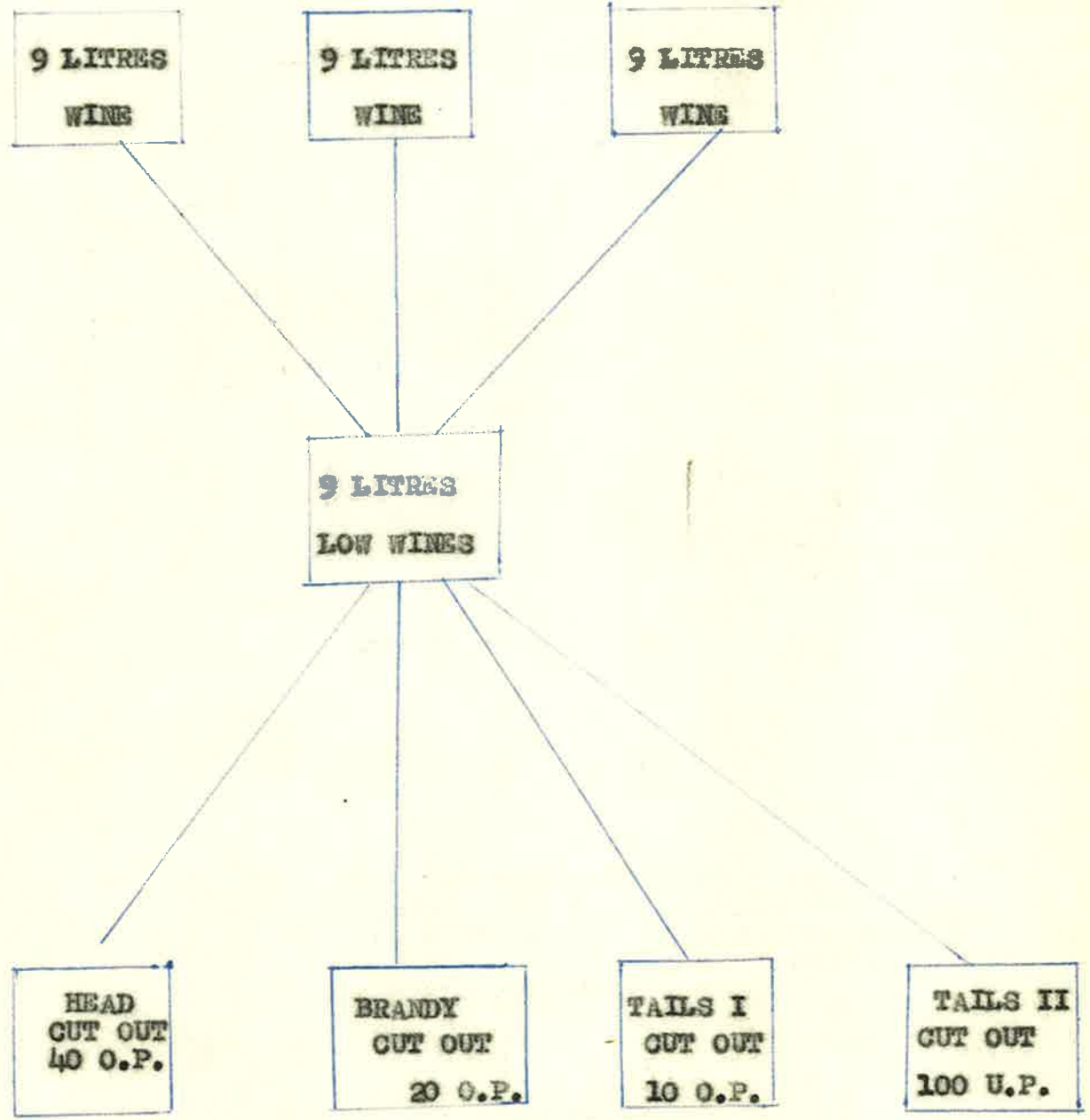
Wines	Alcohol % by Vol.	pH	Sugar	Tot. acid	Vol. Acid	Lactic	Tartaric.
A I	13.1	2.96	2.9	12.5	0.7	0.2	7.4
A II	13.1	2.95	2.8	13.0	0.62	0.3	7.07
B I	13.3	3.96	2.3	5.9	0.02	9.9	2.76
B II	13.3	3.76	2.3	6.0	0.24	0.4	2.8

Analysis of Low Wines and Brandy Fractions.

Fraction	Alcohol				Acids				Aldehydes				Esters				pH			
	A I	A II	B I	B II	A I	A II	B I	B II	A I	A II	B I	B II	A I	A II	BI	B II	A I	A II	BI	B II
WINE	13.1	13.1	13.3	13.3													2.96	2.95	3.96	3.76
LOW WINES	28.4	28.2	30.	32.6	93	95	50	47	11	11	12	13	124	144	164	152	3.77	3.77	3.96	4.02
HEADS	76.6	75.7	77.9	77.5	8	10	7	7	19	19	26	28	266	276	286	331	5.47	5.28	5.8	5.55
BRANDY	72.5	72.9	74.4	73.3	8	7	6	7	4	5	6	7	43	33	35	48	5.22	5.28	5.46	5.3
TAILS I	62.8	64.3	63.7	62.6	14	14	13	14	3	2	4	3	44	5	20	14	4.9	4.86	4.91	4.92
TAILS II	26.5	29.0	28.2	26.8	63	56	50	51	6	4	6	7	42	12	42	32	3.90	3.92	3.95	3.95

PLAN OF DISTILLATION.

Each distillation was carried out as below:—



## DISCUSSION OF RESULTS.

### Wine.

Figures show a slightly lower alcohol content in wines fermented at the low pH which may be attributed to the inhibiting effect on the yeast. This also accounts for the high residual sugar and differences in volatile acidity.

The marked difference in total acidities and tartaric acid levels in the wine is shown. This was aimed at so that any differences in results due to tartaric acid would be clearly defined.

### Distillates.

#### Acids:

Considerably higher values in acids in AI and AII are due both to higher volatile acid produced during fermentation and to carrying over of some non-volatile acids during distillation.

#### Aldehydes:

There is a marked drop in aldehyde formation which is more clearly shown in the difference between "head" fractions, aldehydes being boiled over largely in the early part of the distillation in an open column.

It is probable that there is a slightly lower production of aldehyde during fermentation in an acid medium. Acetaldehyde is a normal product of fermentation in small amounts. In the final stages of fermentation it is said to be converted to alcohol by reduction due to enzyme action. The change in pH would effect the activity of the enzyme and hence the products of fermentation.



In the first distillation to low wines some tartaric acid could be carried over during the boiling and in view of Angove's work (1) it appears that the process of distillation itself has an effect on aldehyde production which varies with different concentrations of tartaric acid or tartrates in the wine.

Esters:

A lower ester formation from the more acid material is shown which is contrary to what would be expected and is difficult to account for. It is quite evident that this acid has no importance in regard to increasing ester production.

Secondary Alcohols:

The only available method sufficiently rapid for this work - that of Girard and Ombiasse - was considered far too inaccurate for the results to be worth presenting. Results were found to vary widely under conditions which were extremely difficult to standardise. The method has been used widely in France, but is subject to severe criticism in the literature. A review of available methods was made and these are presented and discussed in the appendix.

SUMMARY.

A small section of a large field of work has been attempted and it has been found that the concentration of tartaric acid present in the must and wine does have a considerable bearing on aldehyde production. A lower aldehyde concentration in a wine would reduce the head

fraction necessarily removed in distillation.

Time has not permitted further work to complete this investigation and a series of experiments could be devised to examine the problems of base material more closely.

The method used for aldehyde analyses is open to some error and standardization of temperature would be necessary for accurate work.

#### ACKNOWLEDGEMENTS.

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6. Renee and Jean Lafen, Riv. de Vitis, Jan. 26, 1939.
7. R.A.C. notes.

APPENDIX.

Colorimetric Methods for Determination of Fusel Oil or Secondary Alcohols in Distilled Spirits.

1. British Government Lab. Method (Allen's Commercial Organic Analysis V):

The sample is freed from colouring matters and extract by distillation, 120-150 ml. being diluted to 200 ml. with water and gently distilled as far as possible without charring the residue. It is then made to volume and the alcoholic strength determined. Required strength for determination is 50% by volume.

Standard Mixture - 1 gm. of a mixture of propyl alcohol 1 pt., isobutyl alcohol 2 pts., amyl alcohol 3 pts., and capryl alcohol 1 pt., is dissolved in 100 ml. of pure 50% alcohol, this solution being further diluted to contain 0.1 gm. of the mixture per 100 ml.

Estimation:

10 ml. of the distillate treated in a flask with 0.5 ml. of a 1% solution of furfural and then with 10 ml. of conc.  $H_2SO_4$ . This is slowly run in to form a layer at the bottom of the flask.

10 ml. portions of 50% alcohol containing from 0.5 ml. upwards of the standard 0.1% solution of higher alcohols are treated in the same way.

Each flask is placed in an ice-cold water-bath and shaken gently for 30 seconds and then allowed to stand for about one hour at the ordinary temperature.

The production of a reddish violet colour indicates that the sample contains an appreciable quantity of higher alcohols, the amount of which can be estimated by comparison with standards.

2. Gerard and Cuniasse Method (Allen's Commercial Organic Analysis V, Vol.I):

50 ml. Spirit adjusted to 50% absolute alcohol in a 250 ml. flask.

Meta phenylenediamine and a few grains of freshly broke pumice is added and the whole is refluxed for one hour, then distilled collecting as much distillate as possible.

Filled to volume - 50 ml. 10 ml. of this solution then placed in a 100 ml. flask.

10 ml. pure colourless  $H_2SO_4$  then added so that it forms a layer on the bottom of the flask.

The flask is next shaken vigorously and heated over a bunsen until it just boils and is then cooled.

The colour produced is compared with standards.

Standard: A .05% solution of Isobutyl alcohol in 50% purified ethyl alcohol.

Criticism:

Secondary alcohols are considered to be very inaccurately measured by this method. Secondary alcohols in an absolutely pure state, with pure  $H_2SO_4$  in clean glassware, give no colour whatsoever.

3. Komarowsky-Fellenberg Method (Simmond's "Alcohol", 419):

10 ml. of distillate, diluted to 30 per cent of alcohol by volume, and treated with 1 ml. of a 1 per cent alcoholic solution of salicylic aldehyde and then carefully mixed with 20 ml. of strong  $H_2SO_4$ . After 45 minutes the mixture is diluted with 50 ml. of 62 per cent  $H_2SO_4$ . The colour obtained is then compared with those produced in standard mixtures treated in the same manner.

4. Determination of Higher Alcohols in Distilled Liqueurs  
(Penniman Smith and Lawshe, Ind. Eng. Chem.  
9, 91 (1937):

These authors have compared the Allen Marquardt method with a colorimetric method described below and claim that the former, which is the A.O.A.C. method, reports on an average only 60% of the fusel oil in the sample. They state that the A.O.A.C. method is naturally affected by variations in technique and uncontrolled factors such as the temperature at which the extraction is carried out.

The advantages of the colorimetric method are:-

- (1) The time required for the determination is less than by any other method.
- (2) The sensitivity of the method is far greater than any other. By virtue of this fact the colorimetric method is applicable to low proof beverages such as wines and beers, in which fusel oil has not hitherto been determined.
- (3) Abnormal or unusual samples are readily detected by off shades of colour and by the use of two or more colour reagents on the same sample.
- (4) The method yields results of the correct order of magnitude.

Disadvantages stated by the authors:-

- (1) The sample must be given a rigorous pre-treatment to eliminate interfering substances.
- (2) For accurate work it is desirable to use as the colorimetric standard a sample of actual fusel oil of the same type as that contained in the sample.
- (3) The individual alcohols exhibit different colour intensities and the result is therefore dependent on composition of fusel oil. This source of error is very largely, though not entirely, eliminated by the use of fusel oil standards.

Procedure with p-dimethylaminobenzaldehyde or salicylaldehyde.

Place 2.00 c.c. of the distillate, obtained as directed above, in a 125 c.c. Florence Flask. Add 20.0 c.c. of concentrated sulphuric acid, swirling the flask in a bath of cold water during the addition. Then add 2.00 c.c. of a solution of the reagent in 95 per cent. ethyl alcohol (10 mg. per c.c.) again swirling flask in a cold bath.

Prepare a similar flask containing 2.00 c.c. of a standard fusel oil solution acid and reagent.

Place the flasks simultaneously in a bath of vigorously boiling water. After 20 minutes transfer the flasks to the cold bath. When cool add 25 c.c. of (1 - 1) sulphuric acid and mix thoroughly by swirling. The solutions are then ready for comparison in the colorimeter.

Procedure with Vanillin.

Proceed as above for the other two reagents except for the following differences:-

- (a) Use only 10 c.c. of conc. sulphuric acid in making up the reaction mixture.
- (b) The vanillin solution contains 17.5 mg. of reagent per c.c. of 95% ethyl alcohol.

Where a standard fusel oil is not available a satisfactory working standard for colorimetric work can be prepared by mixing isosamyl and isobutyl alcohol in the ratio of 4 : 1.

The percentage of ethyl alcohol in the standard should be approximately the same as in the prepared sample.

A convenient fusel oil conc. is 100 gms/100,000 c.c.

The colour reaction is not peculiar to higher alcohols but unsaturated hydrocarbons to which the higher alcohols

are converted by  $H_2SO_4$ .

Interfering substances which must be removed are aldehydes, ketones and acetals. Acids are not important.

Preparation of the Sample:

Place 25 c.c. of sample in a 500 c.c. round bottomed flask. Add 0.5 grams of silver sulphate and 1 c.c. of (1 + 1) sulphuric acid and make the total volume up to 110 c.c. Reflux gently for 15 minutes. Make the solution alkaline with 5 c.c. of (1 + 1) sodium hydroxide solution and reflux for 30 minutes. Bumping can be prevented by the addition of small quantities of granulated zinc. If foaming occurs it can be reduced by the addition of 15 grams of sodium chloride. The addition of salt results in a partial conversion of silver oxide to silver chloride, but this fact does not appear to affect the efficiency of the silver as a dealdehyding agent.

After the saponification the sample is distilled, 75 c.c. of distillate being collected. This distillate contains all of the higher alcohols originally present in the sample. The concentration has been reduced to one-third of the sample. This reduction in concentration is made necessary by the extreme sensitivity of the colour reagents.

For the colour reaction the following factors must be controlled:-

- (1) The amount of sample.
- (2) Amount of reagent.
- (3) Amount of conc. sulphuric acid.
- (4) Concentration of ethyl alcohol.
- (5) Temperature and time of heating to develop colour.
- (6) Amount of diluent added after terminating the reaction.
- (7) The concentration of sulphuric acid in the diluent solution.

The reaction is not allowed to go to completion but is arbitrarily stopped after a definite length of time by chilling the reaction mixture and diluting. It is therefore necessary to run standards and sample side by side under exactly similar conditions.

SOLVENT Method (Rose, Allen's Commercial Organic Analysis V):

The principle of this method is that certain solvents will absorb secondary alcohols from distilled spirits and hence increase the volume of the solvent.

A specially designed glass container with a graduated tube is used for the determination.

The quantity of the distillate containing exactly 50 or 100 ml. of alcohol is added to the container which already holds exactly 20 ml. of chloroform. Then 2 ml. of 25%  $H_2SO_4$  is added. The tube is well shaken, immersed in a water bath at  $20^\circ$  for one hour, again well shaken and stood upright in the bath till the layers separate. The volume of the chloroform is then read off.

Ethyl alcohol causes a 0.2 ml. increase in volume which must be deducted and each 1% of amyl alcohol causes an increase of .6 ml. Different alcohols give different values. Temperature control is essential.

This method is convenient and rapid. It is satisfactory for crude spirits but unreliable on clean spirits. It is said to give high results compared with other methods. It could be conveniently used commercially.



Methods for higher alcohols which depend on extraction and conversion to some other derivative which can be readily determined.

1. Allen-Marquardt (A.O.A.C. and Allen's Commercial Organic Analysis):

This method is based on extraction of the higher alcohols with carbon tetrachloride and oxidation to the corresponding acids which are estimated by titration.

Method:

200 ml. of sample taken and 1 ml. of strong KOH solution added. The whole is then boiled for one hour under reflux.

The liquid is then transferred to a distilling flask fitted for steam distillation. Steam is not introduced until about 20 ml. are left in the flask. The distillation is so regulated that by the time 300 ml. of distillate has been collected about 10 ml. remains in the flask.

The distillate is mixed with saturated NaCl solution until it has a specific gravity of 1.10 and divided into equal parts so that duplicate determinations may be made. Each part is extracted with 100 ml. of purified  $\text{CCl}_4$  using, 40, 30, 20 and 10 ml. successively.

Some ethyl alcohol is contained in the tetrachloride extract. To remove it, the extract is shaken first with 50 ml. of the saturated salt solution and separated, and then with 50 ml. of a saturated solution of  $\text{Na}_2\text{SO}_4$  to remove remaining chloride.

For the oxidation of the higher alcohols a mixture of 5 gms. of pot. dichromate, 2 gms. conc  $\text{H}_2\text{SO}_4$  and 10 ml. of water is added to the  $\text{CCl}_4$  extract in a flask provided with a reflux condenser and the liquid boiled gently for 8 hours on a water bath. After the addition of 30 ml. of water to the liquid in the flask the contents are distilled until 20 ml. remain.

The residue is then steam distilled as in the first operation until little more than 5 ml. remain after 300 ml. of total distillate has been collected.

The distillate is then titrated with decinormal barium hydroxide solution, shaking thoroughly after each addition until neutral to methyl orange; phenolphthalein is next added and the titration continued to the neutral point.

Each ml. of the decinormal solution required in the phenolphthalein stage of the titration represents 0.0088 gm. of higher alcohols calculated as amyl alcohol.

This method has been criticised in an article by Bedford and Jenks (J. Soc. Chem. Ind. 1907, 26, 123.) It gives low results as follows:-

<u>Alcohol.</u>	<u>Found % of quantity added.</u>
Amyl	93-110
n-Butyl	30-70
Isobutyl	26-52
n-Propyl	13-21

The method is too long for commercial use and liable to large errors unless carefully carried out in every detail. Bardy's method (Allen's Commercial Organic Analysis V) is similar to this but uses esters instead of acids.

## 2. Determination of Fusel Oil by Alkaline Permanganate.

(A.S. Mitchell and C.R. Smith, U.S. Dept. Agr. Bur. Chem. Bull. 122, 199):

A study of the conditions necessary to produce definite oxidation of various alcohols by alkaline  $KMnO_4$ . Object, to avoid prolonged digestion and subsequent distillation with attendant concentration of oxidising mixture. Results of preliminary experiments, using amyl alcohol showed that

oxidation is quantitative at 0°C and at higher temperatures the yield of valeric acid is decreased.

A direct volumetric method was found possible after the satisfactory conditions for oxidation had been determined. A known amount of H<sub>2</sub>O<sub>2</sub> mixed with H<sub>2</sub>SO<sub>4</sub> was used for oxidation and the excess H<sub>2</sub>O<sub>2</sub> titrated. Best results were obtained by oxidising for 10 minutes at 0° and then warming for 20 minutes up to 25°.

3. Determination of Amyl Alcohol in Distilled Spirits.  
(S.T. Schick Tanz and A.D. Etienne, Ind. Eng. Chem, July, 1939):

In this method the fusel oil is separated by distillation and subsequent extraction with carbon tetrachloride. It is determined by esterification with acetyl chloride.

Reagents:

0.23 M solution of acetyl chloride in dry toluene.

0.5 M solution of pyridine in dry toluene.

Apparatus:

Allen Marquardt distillation unit.

A specially constructed dehydration and dealcoholizing still to remove the ethyl alcohol and water from the carbon tetrachloride extracts. Described and illustrated in the reference given above.

Method:

The sample is distilled with caustic soda. The distillate is then shaken with sodium chloride and extracted four times with carbon tetrachloride. The extract is then placed in a special reaction flask and attached to the dehydration still.

After cooling, the carbon tetrachloride solution is treated with pyridine and acetyl chloride and shaken on a

water bath at 60<sup>0</sup>C. for 30 minutes. It is then cooled and treated with excess 0.100 N sodium hydroxide and back titrated with 0.100 N H<sub>2</sub>SO<sub>4</sub>.

One ml. of 0.1 N sodium hydroxide is equivalent to 0.0088 gram of fusel oil as amyl alcohol.

Propyl alcohol is not determined by this method, being lost in the second distillation.

#### Methods based on Refractive Index.

Two methods for refractive index measurement of higher alcohols were found in the literature -

W. Leithe (Z. Unters Lebensm., 1936, 72, 351, 354.)

S.T. Schicklitz and A.D. Etienne and W.I. Steele

(Ind. Eng. Chem. Anal. Ed. 11, 420-2, 1939)

Both of these methods are based on the extraction of the secondary alcohols by a solvent, prior to measurement of refractive index. They are both open to the criticism of inaccuracy owing to the difference in composition of samples.

#### SUMMARY.

Examples of the main types of methods are given and others are simply modifications of these. There is no method which is entirely satisfactory for accurate work. The Rose method could be developed and appears to be the most satisfactory for commercial use. All colorimetric methods are unsatisfactory for general use owing to the difficulty of obtaining a true standard for comparison.

The method of Schicklitz and Etienne (Ind. Eng. Chem. July, 1939) appears to be conveniently rapid, but requires

special apparatus and does not determine propyl alcohol.  
It is probably the most satisfactory method available.

Ester determinations:

During the experimental work it was found that by standing the sample overnight with NaOH before titrating, results were obtained which compared very favourably with the refluxing procedure. This means a considerable saving of time in dealing with a large number of samples.

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