ACIDITY MODIFIES BRANDY COMPOSITION

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SYNOPSIS :-

1. By reducing pH of base wine the ester content of brandy is increased.

2. Returning "heads" and "tails" from the brandy run to the next low wine charge causes an increase in esters, especially at pH 3.

3. Reducing the pH with sulphuric acids, besides being more economical, gives a higher ester content than tartaric acid, and at the required strength has no adverse effect on copper plate.

INTRODUCTION :-

Australian brandies are of reasonably high standard, but have not attained to the quality of French Cognacs, and as our brandy industry is relatively young, it calls for investigation, the aim being better quality.

The purpose of my project is to show that by reducing the pH of brandy base wine results in an increase in esters, which are essential component of good brandy.

In direct comparison to our base wines, cognacs are distilled from highly acid base wines, and the principle difference in Australian and French brandy analysis lies in the ester level, the French spirits tending to be higher.

Our climatic conditions do not lead to high acid wines as in France, and thus we can only rely on reduction of pH, after fermentation, if we wish to increase the ester content of our brandies.

GENERAL REVIEW OF LITERATURE :-

1. DISCUSSION :

Literature pertaining to my project is relatively scarce, as very little work has been attempted on grounds of reducing pH of base wine.

Graham (1) states increased concentration of acid gives an increased ester content.

To show the difference in ester content of cognacs and Australian brandies, a study of the cognacs should be helpful.

From Raves (ii) the term cognac, in France, can be legally applied only to the brandy produced in a limited area, and every effort is made to safeguard the name and reputation of this product, which is known and imitated the world over.

The cognac producing areas of France comprise almost the whole of the south-eastern section of the country.

The Charentes and Armagnac constitute the central portion of the section. The finest brandies "Fines Champagnes" and "Cognac" are products of the distillation of the wines of Charentes. The main varieties used for distillation wine are Folle Blanche, Colombar, and Saint Emilion, the latter being synonymous with our White Hermitage.

It is noticeable the three main varieties are white, which are considered to be superior to red owing to less oils contained in skins and stems. Charentes, the main cognac area enjoys a maritime climate without any great extremes of temperature. The winter is moderately sever, rainfall extremely high, averaging 47.6 inches per annum, it falls frequently and in small amounts. August and September, the months when the berries fill and ripen are the driest of the year, thus the grapes mature under favourable conditions. The natural conditions become progressively less favourable.

to the north and to the south of Charentes indicating the special importance of the climatic factors in growing vines suitable for distillation of high quality brandy.

We in Australia cannot compare our climatic conditions with those of France, but in studying the analysis of young French cognacs in Girard and Cuniasse, it is obvious they contain a much higher ester level than our brandies (analysis from Commonwealth Dept. of Chemistry (IV).) The following is analysis of renowned Commercial cognacs from (III)

	Esters
1 year Cognac	97.5
2 " "	88
3 " "	69.5
4 " "	71.1
Fine Champagne	74.8

From (IV) 23 samples of South Australian brandies obtained from various wineries, and analysed in Department of Chemistry.

73	26	24	46
75	134	46	85
35	51	39	40
43	29	75	40
74	71	93	25
24	41		19

Conference of interested parties recommended following standard, 40 - 80 esters expressed as grams/100,000 pts. A.A. (Absolute Alcohol)

From Angove (5) we get a comparison between Australian and French brandies, but incorporating run-back of heads and tails.

Brandy Section	Ester Aust.	French.
A.	43	141
B.	45	132
C.	48	96

Certain importing countries require a brandy containing not less than 60 grams ester as ethyl acetate per 100,000 parts of Absolute Alcohol, from above analysis it is seen that many Australian brandies do not attain this level.

2.   RUN - BACK :

From Rocques (VI) the usual procedure in the Charentes, that appears best for the production of superior quality, consists in making two successive distillations, known as the system of "brouillis" with "repasse".

It is the traditional method that the Charentes have always considered the best and this they use when they wish to produce quality brandy.   The distillation is carried out as follows :-

The wine in its lees is placed in the boiler of the still, and is heated cautiously till the wine boils.

The first distillate is of 60 to 65° (alcohol by volume) and has the characteristic odour of aldehyde.   The alcoholic content rises very rapidly to 70 - 75° and the distillation is continued until the alcoholometre shows zero. This happens when about a third of the liquid has distilled, and the product is termed the "brouillis" (low wines).

The "brouillis" passes to the "repasse", which is essentially, a rectification of the "brouillis", this being to cognac what industrial columns are to neutral alcohols.

The products of the head are put to one side, in an amount that varies with the nature and quality of the wines, and represents about 5% of the brandy.   These heads are mixed with the next brouillis.

The brandy, which now begins to run is at 80 - 85° and it is collected until it falls to approximately 50° and the brandy collected is at 66 -70°.

The distillation is continued until the liquid drops to zero.   The liquid received during this stage is termed "secondes" (tails), and shows 20 - 24° of alcohol.

It is, in general, mixed with the next wine distilled. However, when the wine is rich in alcohol, many distillers fraction the "seconde" - the portion running from 50 to 20° is mixed with the brouillis, and the part from 20 - 6° with the wine to be distilled.

This procedure adopted in Part II of project, i.e. fractionating the tails.

Rene and Jean Lafon (VII) and Elliott (VIII) both also emphasise the run-back as being characteristic of French procedure.

3. <u>SULPHURIC ACID</u> :

Has been found preferable to use sulphuric acid in lieu of tartaric, not only for economy, from (VI) price of H_2SO_4 3d. a lb. against 4/6d. a lb. for tartaric, but also because it gives superior results.

H_2SO_4 has a lower pKa value than tartaric acid.

		pKa
H_2SO_4	1st H	completely ironised
	2nd H	1.52
Tartaric acid	1st H	3.01
(H_2T)	2nd H	4.05

H_2SO_4 being more highly ionised will react with the potash neutralising the tartaric acid, forming K_2SO_4 and releasing tartaric acid

$$H_2\bar{\bar{T}} + 2KOH \longrightarrow K_2\bar{\bar{T}} + 2H_2O$$

$$K_2\bar{\bar{T}} + H_2SO_4 \longrightarrow K_2SO_4 + H_2\bar{\bar{T}}$$

Thus reducing the pH with H_2SO_4 increases the content of tartaric acid.

EXPERIMENTAL.

Apparatus and Material : -

    1. The Still - quick-fit glass still, with two litre
        and four litre boiler, heated by an electric hot
        plate, with heat regulator.

    2. Wine - 20 gallons of 1947 Pedro Sercial blend.
           20 " " 1947 Pedro.

          Blended to give 19% Proof Spirit

    3. Normal Tartaric acid, sulphuric acid, and potash
        for adjusting pH.

Methods of Analysis :-

    Alcohol - Pycnometer bottles, and Sykes hydrometers.

    Acids - direct titration (phenolphtraldin) parts of
acetic acid per 100,000 parts absolute alcohol.

    Esters - A.O.A.C. (IX) expressed as parts ethyl acetate
per a00,000 parts absolute alcohol, but reflux 15 minutes
(2 hours - A.O.A.C.)

    Aldehydes - Jaulmes and Expezel (X) parts acetaldehyde
per 100,000 parts absolute alcohol.

    Secondary alcohols - Girard and Cuniesse (III). See
Appendix A for modification.

EXPERIMENTAL.

PART I.

EFFECT OF pH ON LOW WINES COMPOSITION.

1. Standardised enough wine at pH4, using KOH (Potash).
Adjusted pH with H_2SO_4 and $H_2\overline{T}$ (tartaric acid) to pH 3.5 and
pH 3 in each case.

Adjusted to volume 725 mls. with H_2O to give same
alcohol content.

Distilled 500 mls which contains all alcohol, therefore
all distillates have same alcohol content.   Alcohol at each
pH by Pyonometer bottle giving Sp. G.   For statistical pur-
poses, three distillations at each pH and six at pH4 and all
distilled to standardised procedure.

TABLE OF ANALYSIS

WINE pH 3.75   BLENDED PEDRO & SERCIAL 1947.

	pH raised with KOH pH 4	pH reduced with H_2T pH 3.5	pH reduced with H2SO4 pH 3.5	pH reduced with H_2T pH 3	pH reduced with H₂SO4 pH 3.
Esters	102 95 100 93 90 96	119 119 111	111 123 135	127 119 119	127 135 135
Acid	67 57 67 66 57 63	66 69 68	63 76 63	69 69 72	69 69 69
Aldehydes	9 11 14 14 12 14	12 14 17	9 14 12	11 11 12	13 12 14
Secondary Alcohols	104 76 104 93 93 80	76 93 72	93 69 67	93 137 93	76 88 80

Expressing results statistically confirms the hypothesis that the lower values of pH give more esters, as under. Although a significant difference between the two acids, statistically it may be due to chance.

EFFECT OF LOWERING pH ON THE ESTER CONTENT OF BRANDY.

	Acid		Total
	$H_2\bar{T}$	H_2SO_4	
4.0	102 95 100 297	93 90 96 279	576
pH 3.5	119 119 111 349	111 123 135 369	718
	127 119 119 365	127 135 135 397	762
TOTAL	1011	1045	2056

	Acid.		Total
	$H_2\bar{T}$	H_2SO_4	
3.5	349	369	718
	365	397	762
TOTAL	714	766	1480

i. (including zero acid treatment)

II. (omitting zero acid treatment)

iii. **Treatment Totals** (No. of replications shown in red)

Nil $H_2\bar{T}$ (3.5) H_2SO_4 (3.5) $H_2\bar{T}$ (3.0) H_2SO_4 (3.0)   Total

576 [6] 349 [3]   369 [3]   365 [3]   397 [3]   2056 [3]

Table I :-   Total S.S. $= 102^2 + 95^2 + \ldots + 135^2 - \dfrac{2056^2}{18} = 3901.18$

Table III. :-

Between treatment S.S. $= \dfrac{576^2}{6} + \tfrac{1}{3}(349^2 + 369^2 + 365^2 + 397^2) - \dfrac{2056^2}{18} = 3387.11$

therefore within treatment S.S. $= 3901.18 - 3387.11 = 514.07$
The treatment S.S. can now be partitioned into 3 components, viz. S.S. due to pH, S.S. due to acid, S.S. due to pHX acid interaction.

Table I :-

S.S. due to pH $= \frac{1}{6}(576^2 + 718^2 + 762^2) - \frac{2056^2}{18} = 3149.78$

Table II :-

S.S. due to acid $= \frac{1}{6}(714^2 + 766^2) - \frac{1480^2}{12} = 225.33$

Table II :-

S.S. due to pH X acid interaction.

$= \frac{1}{3}(349^2 + 369^2 + 365^2 + 397^2) - \frac{1480^2}{12} - \frac{1}{6}(718^2 + 762^2) -$

$\frac{1480^2}{12} - \frac{1}{6}(714^2 + 766^2) - \frac{1480^2}{12} = 12.00$

The S.S. due to pH can be further partioned into a linear component and a quadratic component by means of orthogonal polynomials.

Total Ester content

at pH	= 4.0	576	− 1	1
" "	= 3.5	718	0	− 2
" "	= 3.0	762	1	1

(a) Linear regression coeff. $= b_1 = \frac{762 - 576}{2 \times 6} = \frac{187}{12}$

$= 15.50$

Var. $(b_1) = \frac{39.54}{12} = 3.30$

S.D. of $b_1 = \sqrt{3.30} = 1.82$

Therefore $b_1 = 15.50 \pm 1.82$ units of ester content / 0.5 decrease in pH.

And S.S. due to linear regression $= \frac{186^2}{12} = 2883.00$

(b) Quadratic regression coeff. $= b_2 = \frac{762 - 2 \times 718 + 576}{6 \times 6}$

$= -\frac{98}{36}$

$= -2.72$

Var. $(b_2) = \frac{39.54}{36} = 1.10$

S.D. of $b_2 = \sqrt{1.10} = 1.05$

Therefore $b_2 = -2.72 \pm 1.05$ units of ester content / 0.5 decrease in pH./ 0.5 decrease in pH and S.S. due to quadratic regression $= \frac{(-98)^2}{36} = 266.78$

ANALYSIS OF VARIANCE.

Variation due to		D.F.	S. S.		M. S.	RATIO	RATIO
	Linear req.	1		2883.00	2883.00		**** 72.91 ****
pH		2	3149.78		1574.89	39.83	
	Quad. req.	1		266.78	266.78		6.75 *
between treat-ments		4	3387.11				
	acid	1	225.33		225.33	5.70*	
	Interaction pHX acid	1	12.00		12.00	—	
within treatments		13	514.07		39.54		
TOTAL		17	3901.18				

To test the difference between two means.

	Tartaric Acid	H_2SO_4
	102	93
	95	90
	100	96
Total	297	279
Mean	$99 = \bar{x}_1$	$93 = \bar{x}_2$

$$s^2 = \frac{(3^2 + 4^2 + 1^2) + (0^2 + 3^2 + 3^2)}{2 + 2} = \frac{44}{4} = 11.$$

Therefore $V(\bar{x}_1) = \frac{11}{3}$, $\qquad V(\bar{x}_2) = \frac{11}{3}$

$$V(\bar{x}_1 - \bar{x}_2) = V(x_1) + V(x_2) = \frac{22}{3} = 7.3$$

therefore $t = \dfrac{(\bar{x} - \bar{x})}{\sqrt{V(\bar{x}_1 - \bar{x}_2)}} = \dfrac{6}{\sqrt{7.3}} = 2.22$ with 4 D.F.

Fitting Linear & Quadratic Regressions to the Data.

Linear regression gives

Ester content at pH = 4.0 to be 685.33 - 15.50 x 6 = 592.33

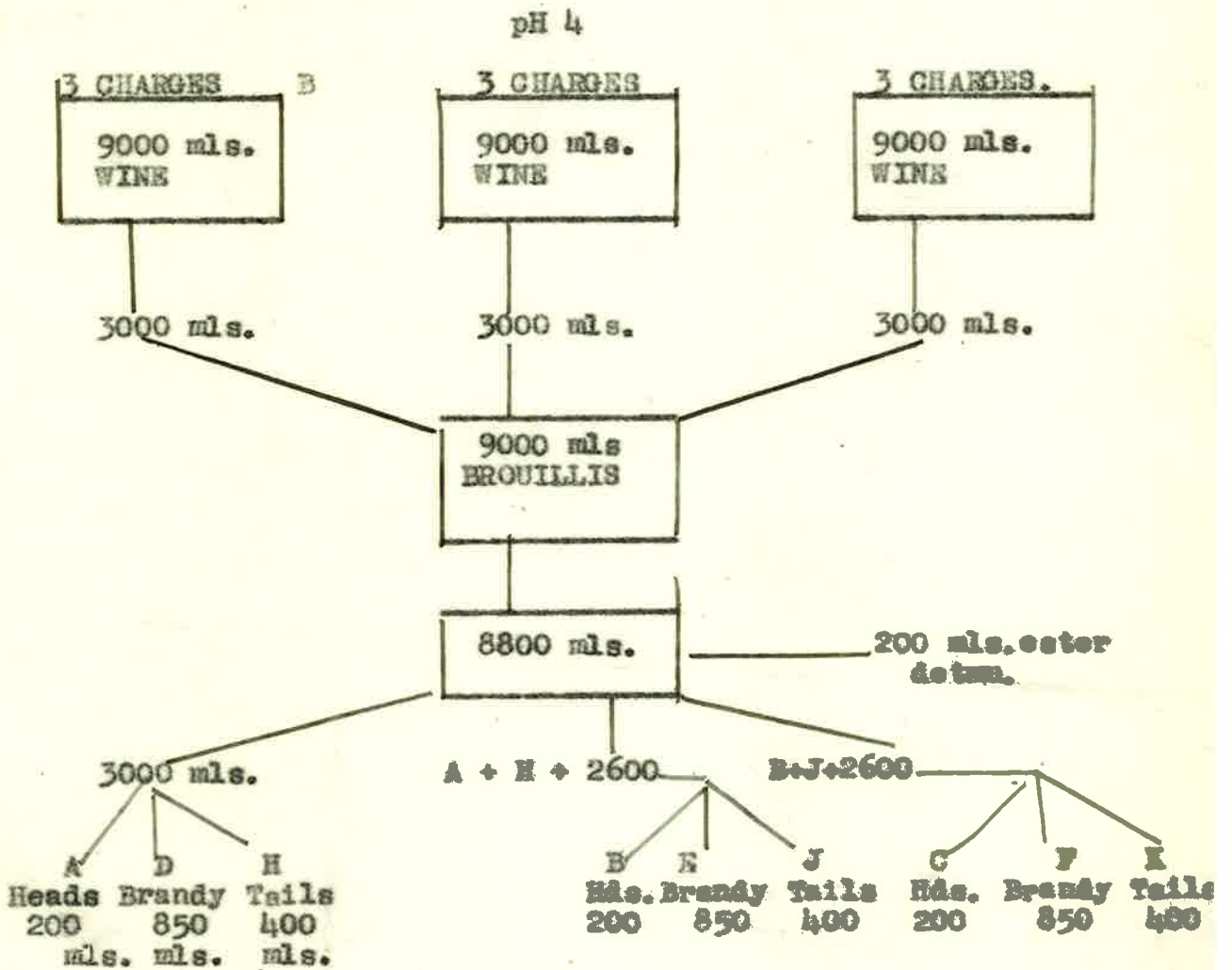"   "   " "   3.0 "   " 685.33 + 15.50 x 6 = 778.33

Plotting these points and putting in the straight line and the curve approximately we see how the rate of increase of ester content with decreasing pH alters.
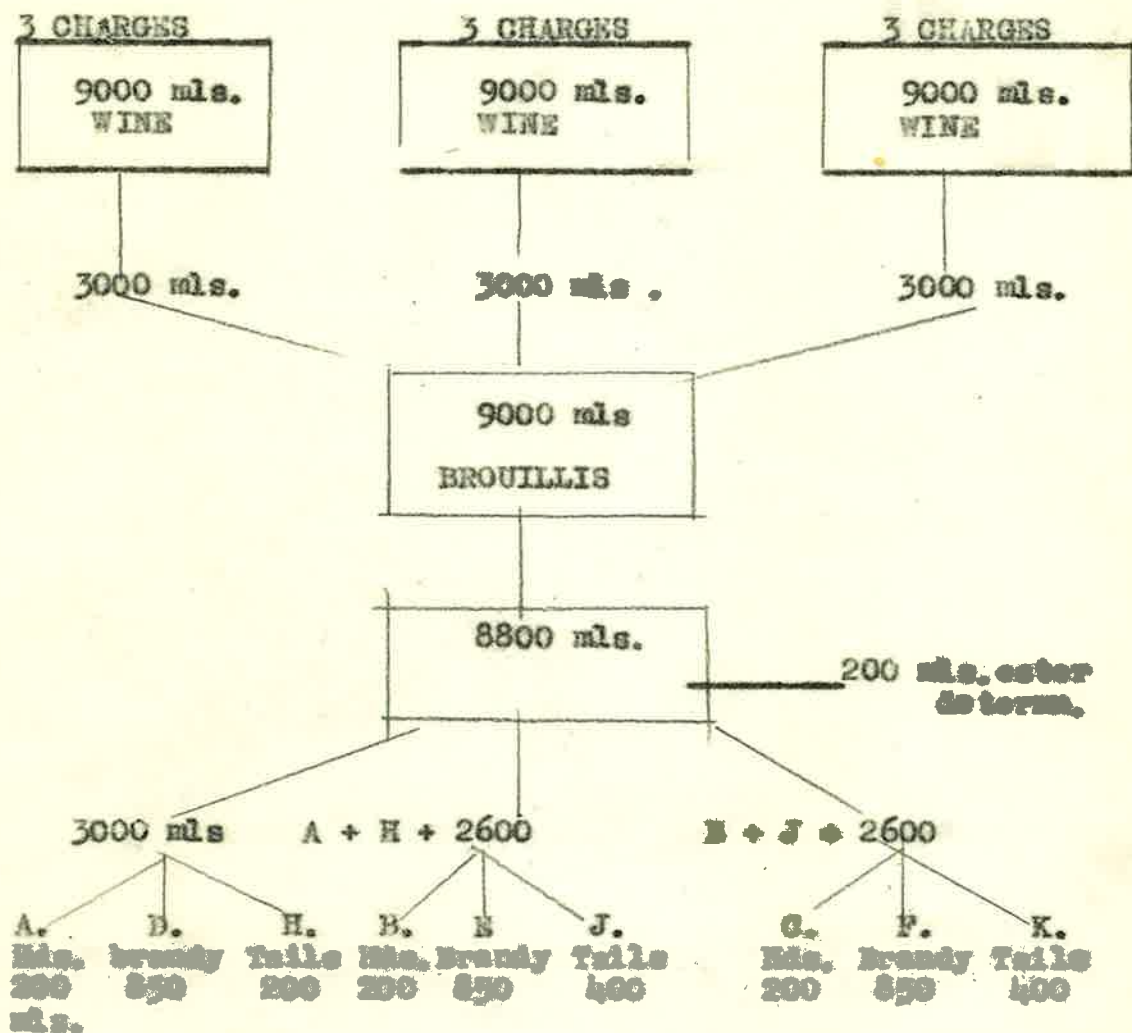
Graph

Part II.

Survey and analysis of distillation incorporating "run-back".

Each distillation consisted of a 3 litre charge.

pH 4

Heads and tails seperated by nose, and tails cut out at 20°, equal amounts taken in each case to standardise procedure.
Ester determinations on low wines, and on all fractions.

pH 3 reduced with H_2SO_4

3 CHARGES	3 CHARGES	3 CHARGES
9000 mls. WINE	9000 mls. WINE	9000 mls. WINE

3000 mls.　　　　3000 mls.　　　　3000 mls.

9000 mls BROUILLIS

8800 mls.　　　　　　　200 mls. ester determ.

3000 mls　　　A + H + 2600　　　E + J + 2600

A. Mls. 200 mls.	D. brandy 850	H. Tails 200	B. Mls. 200	E. Brandy 850	J. Tails 400	G. Mls. 200	F. Brandy 850	K. Tails 400

pH3 reduced with Tartaric Acid.

(as above)

Table of Analysis shewing effect of pH on esters during
"run-back".

Low Wines

pH		Esters
4		149
3 reduced with H_2SO_4		164
3 reduced with $H_2\overline{T}$		164

Run-Back

pH	Heads			Brandy			Tails		
	A	B	C	D	E	F	H	J	K
4	106	111	128	52	66	69	89	86	86
3 red. with H_2SO_4	280	360	390	59	78	96	90	70	70
3 " " $H_2\overline{T}$	214	306	360	58	72	78	90	90	89

Reduction in pH clearly shows increased ester content, with
sulphuric acid giving superior results to tartaric acid.

Part III.

Distillers may be dubious of the value of sulphuric
acid for fear of its action on the still.

Following experiment proves H_2SO_4 may be used safely
at the required strength.

Cu plating weighed accurately, and refluxed for 120
hours in wine at pH 2.8, reduced respectively from pH 4 with
H_2SO_4 and $H_2\overline{T}$.

Wt. of Cu. plate	=	9.4611 grams
Refluxed with H_2SO_4, new wt.	=	9.4448 "
Loss in wt. due to H_2SO	=	.0163 "

Wt. of Cu. plate $\qquad$ = $\qquad$ 9.5711 grams

Refluxed with H_2T, new wt. $\qquad$ = $\qquad$ 9.5462 "

Less in wt. due to H_2T $\qquad$ = $\qquad$ .0249 "

From the above results, H_2SO_4 has less adverse effect on Cu, than H_2T.

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SUMMARY and CONCLUSION.

PART I.

Referring to table of analysis, page 7, reduction of the pH of brandy base wine has no significant effect on secondary constituents, other than esters, thus after part one, only analysis of esters was carried out.

PART II.

The behaviour of the ester content in the distilled spirits shows that as the concentration in the wash increases, the tendency is for a marked increase in the resultant heads, and to a lesser degree an increase in the brandy run, whilst the esters in the tails diminish or remain steady.

PART III.

Although H_2SO_4 has been termed the "acid find" for reducing the pH of brandy base wine, it is here alone useful. H_2SO_4 could not be applied to marketable wine for the same purpose, as the legal limit of sulphate in wine is 2 grams per litre expressed as K_2SO_4.

$$K_2T \quad H \; SO \; \underline{\quad\quad} \; K_2SO_4 \quad H_2T$$

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APPENDIX   A.

SECONDARY ALCOHOLS :

After determining secondary alcohols on samples one and two, modifications to Gerard & Guniasse method found to be necessary to obtain standardised procedure.

Prepared secondary alcohol distillates for colorimetric determination with Dubose colorimeter.

It was found that heating samples gave increased colour, and repeated heating finally caused charring.

Two samples 3 and 4 treated and results on Dubose as under :

	Time of Boiling	Standard	Unknown.
Spirit 3	20 secs.	10	34
	30 "	10	13
	40 "	10	10
	50 "	10	10
Spirit 4	20 "	10	46
	30 "	10	31
	40 "	10	21
	50 "	10	13

To obtain consistency boiled five samples of same strength for 10 seconds, and compared colours with colorimeter. Samples .05% iso-butyl alcohol.

Samples.	Standard	Unknown
1	30	21
2	30	21.5
3	30	24
4	30	22.5
5	30	23.5

Consistency obtained, as difference quite within bounds.

A second batch of five samples, .025% iso-butyl alcohol, boiled for 10 seconds.

Samples	Standard	Unknown
1	30	10.4
2	30	10.7
3	30	12.2
4	30	11.8
5	30	12/4

Thus established, if time of boiling standardised accurately, consistency of results will be obtained.

APPENDIX B.

Traditional method in France, is three or even four charges of wine to give one charge of low wine.   French base wines are of lower alcholic strength than ours, and from following work appears that investigation into number of charge of wine to produce one charge of low wines, is necessary.

Distilled 3 litres of wine at 10% Proof and collected distillate in lots of 100 mls.

Tested each lot with ebulliometer, and was found necessary to collect 1500 mls. to obtain all alcohol.

To observe difference in brandy run, distilled

A.   9000 mls. of wine collecting 3000 mls low wines, i.e. 1 charge of low wine from 3 charges of wine.

B.   6000 mls. of wine collecting 3000 mls. low wines, i.e. 1 charge of low wine from 2 charges of wine.

DISTILLED

A.   Low wines, and collected spirit in 50 ml. lots, and collected 1850 mls. from 3000 mls. to obtain all spirit.

B.   Low wines, and collected spirit in 50 ml. lots and collected 1500 mls. from 3000 mls. to obtain all spirit.

Tested organoleptically spirit of low wines A. and
B.

Oenology colleagues plus Mr. A. R. Hickenbotham
aided this examination.

| A (9000 mls. wine | | | | | B. (6000 mls. wine | | |
| 3000 mls. low wine | | | | | 3000 mls. low wine | | |
mls.	Hds.	Brandy	Tails			Hds.	Brandy	Tails
50)		Hickenbotham)			50)		Collett)	Hicken-
		Stanford	) Hds.				Dolan)	botham
100) Heads		Broderick	) Collett 100) Hds.				Herbert)	Stanford
		Tunnel	) Dolan				Broder-)	Basedow
150)		Basedow	) Herbert 150)				ick)	Tunnel
200			)		200			
250			)		250			
300					300			
350					350			
400					400			
450					450			
500	Tails Commence - Unanimous				Tails commence - Unanimous			

All examiners favoured A as being the best brandy
spirit, but as base wine high in SO_2 differentiation
difficult, and results indefinite.

Calls for further investigation on a larger scale.