

KARL WEIDENHOFER

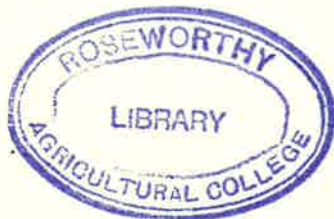
"Suitable methods of testing commercial spirit and  
the results obtained in testing a representative  
group of commercial samples."

Project submitted by -

Chas. W. Kelly

February 14th, 1938.

(not completed)



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## INTRODUCTION:

The analysis of fortifying spirits has been, prior to this last decade, much neglected in this country, partly because little attempt was made to draw up a systematic scheme for their examination, but more particularly because no further control over the sale, or quality, of spirit was exercised beyond that which related to their alcoholic strength.

The importance of good quality spirit in the manufacture of wine has long been recognised, and it is a known fact that large variations in the quality of the finished wine can be brought about by the use of inferior quality fortifying spirit - the method used for assessing the "quality" of a fortifying spirit in the past, by distillers and winemakers, being made by taste and smell, and not by chemical analysis.

If a neutral spirit is used for fortifying a wine, minimum amounts of secondary impurities are introduced, and thus the maturation of the final blend is not impeded by unmellowed spirit constituents, and the wine becomes palatable and wholesome at a very early age. On the other hand if the wine is to be aged in wood for a number of years before going into consumption, then a fortifying spirit with much more character could be used, and such a spirit is, in fact, preferred to a neutral spirit in Portugal. Under these conditions, the secondary constituents contained in the fortifying spirit have time to undergo such changes as esterification and etherification, the products of which confer valuable properties on the finished wine and greatly enhance its market value.

The patent, or fractioning still, is practically the key to the situation as regards the quality of fortifying spirit. As is well known to chemists, this ingenious apparatus produces a very strong and practically featureless because pure, spirit. It separates certain bye products

of fermentation during the distillation process, with the result that when the spirit is highly rectified, it is very pure and free from characteristic odour and flavour.

The simplest form of still, or pot still, which is used in the production of brandy and low strength spirit, yields, on the other hand, a more or less impure spirit, owing partly to the formation of secondary products of fermentation, and partly because of bodies formed during distillation, which, "coming over" with the spirit, impart to it a flavour and odour characteristic of the material used in the fermentation. It is only in pot-still spirit that these products occur to any extent, amongst which may be reckoned compound esters, aldehydes, furfural and fusel oils (higher alcohols); they should be nearly, if not entirely, eliminated in patent or rectified spirit, according to the degree of rectification, and such a spirit is known as "neutral" or "silent" spirit.

During recent years, the Customs Department, realising the importance of using a high quality spirit in the fortification of our Australian bulk wines, caused Regulation 85 to be formulated which deals solely with the type of spirit to be used, viz.- "the spirit must be approved by the analyst and be pure wine spirit of a strength not less than 30 degrees overproof. It shall contain not more than 4 grammes of higher alcohols (calculated in terms of isobutyl alcohol) nor more than 75 mgms of aldehydes (as acetaldehyd) nor more than 5 mgms of furfural per litre of absolute alcohol."

However this regulation has never been observed, and Messrs. Gunn & Gollin <sup>(1)</sup> in 1931 recommended, in their report to the Federal Viticultural Council, that it be enforced, in order that the quality of all fortified wines, and bulk fortified wines for export and home consumption in particular should be raised to a higher standard.

In this paper, I do not propose to discuss the type of spirit required for fortification, as this solely depends upon the class of wine to be made. Suffice to say that should

the wine be destined for early consumption as are our export wines, then the fortifying spirit must be as neutral as possible. However, a "hard" spirit, which contains varying amounts of secondary constituents, is desirable for some high quality wines which will be matured for a number of years in wood.

Our knowledge of some of these ingredients of spirit is imperfect, and it is generally admitted that each of the procedures, so far proposed for their estimation, is lacking in some particular which renders it unsuitable either for routine spirit examination or for assessing the quality of the spirit. The object of the present investigation is to determine suitable methods which are both reliable and, if possible, rapid, for the testing of fortifying spirits, so that distilleries will be able to analyse their products and thus improve the quality of their spirit by varying the conditions of distillation to the requirements of the winemaker.

#### ALCOHOLIC STRENGTH.

The alcoholic content of spirit for fortifying wine is a most important consideration, for it is on the basis of the alcohol content that the article is valued from the Excise and distillery point of view.

It is the usual practice to ascertain the strength of rectified spirits by means of a Syke's brass hydrometer, using an arbitrary scale; This is the method used by the Custom's Department, and it has been universally adopted by wineries and distilleries throughout the Commonwealth. However, there are two major errors arising out of the use of such an instrument,

Firstly, a brass instrument, although standardised, and even if containing a certificate of its accuracy, rapidly changes in weight, due to corrosion and wear of the metal, and an apparently perfect instrument may be many degrees out; this error can be eliminated by the use of a glass instrument, which is not susceptible to such changes in weight. The second error

Is that the instrument is constructed to give the same result as percentage proof spirit in the same sample, at any temperature within the table. Hence a sample 20<sup>O.P.</sup> at 55<sup>O.F.</sup> is still 20<sup>O.P.</sup> at 75<sup>O.F.</sup> but 100 galls. at 55<sup>O.F.</sup> becomes almost exactly 101 gallons at 75<sup>O.F.</sup> thus at 55<sup>O.F.</sup> the equivalent is 120 proof gals. but at 75<sup>O.F.</sup> the equivalent is  $101 \times 120 \div 100 = 121.2$  pf. gals.

Proposals have been made to correct this latter error, but it was not thought sufficiently serious. Legally, it cannot be allowed for, since the error is inherent in the 1880 Act which was re-enacted in 1916, and the following definition was adopted - "Spirit shall be deemed to be of the strength shown by the Sykes hydrometer."<sup>(2)</sup>

ESTERS:

It is generally assumed that the chief ethereal salt present in spirit is ethyl acetate, but it is known that other esters occur, amongst which are compounds of caprylic, capric, butyric and caproic acids. The esters exist in very notable proportions in brandy, and contribute greatly to the "bouquet" of these spirits: ethyl acetate in large quantities can be disagreeable and arrive from the distillation of a "pricked" wine, but in fortifying spirit esters should be absent, or present only in very minute quantities.

In carrying out the saponification process with a view to determining the compound esters present in spirit it should be borne in mind that aldehyde and furfural are not without effect upon the alkali used. Allen<sup>(3)</sup> finds that the estimation of the esters was liable to be effected by the presence of aldehyde and furfural, which neutralised more or less alkali. Furfural appearing to react with a constant ratio of alkali as  $2 \text{ C H O} + 5 \text{ 4 2}$  NaOH -- Na  $\text{C H O} + \text{C H O}$  but aldehydes do not give an  $\text{5 3 2} \quad \text{5 6 2}$  invariable factor. Allen has therefore suggested the removal of aldehydes by boiling the spirit under a reflex condenser for two hours with phosphate of ainline - 1 m.l. of ainline + 1 m.l. of phosphoric acid, 1.442 sp.gr - before distillation.

P. Schidrowitz found that Hewitts reagent (4) - the sodium

salt of phenyl-hydrazine para-sulphonic acid- was more satisfactory, limiting the reflux to 1 hour.

Vasey <sup>(5)</sup> states that the addition of metaphenylene diamine hydrochloride, 2 grms per 500 m.l. of spirit, is very effective when a distillate free from furfural is desired.

The esters are then determined by saponification, being hydrolysed with alkali which combines with the liberated acid.

METHOD:

200 m.l. of the sample is refluxed for 1 hour with 1 gm of metophenylenediamine hydrochloride, or the sodium salt of phenylhydrazine parasulphonic acid 25 m.l. of water is then added and the sample is distilled collecting about 180 m.l., using a mercury valve to prevent loss of volatile substances. Make up to 200 m.l. at the same temp. as the original sample was measured.

Should any acids pass over these are exactly neutralised in 50 m.l. of the Distillate with  $\frac{N}{10}$  alkali and a measured excess of 25 m.l. of  $\frac{N}{10}$  alkali added. Then boil for 10-15 mins. under a reflux condenser, care being taken to prevent any bumping or the most volatile constituent - the esters - will be lost. All "official" methods for the determination of esters in alcoholic liquids agree that the refluxing of the spirit with excess of hot alkali should continue for 1 hour. Allen <sup>(6)</sup> suggest that the time be reduced to 30 minutes, while Hossack <sup>(7)</sup> states that even this shorter time greatly exceeds what is analytically necessary and recommends refluxing for 10 mins; and he points out that for a busy analyst the waste of 50 minutes, with the corresponding "tie up" of apparatus and bench space for each sample, is a serious matter.

After refluxing, the sample is cooled, an excess of  $\frac{N}{10}$  acid added and then back titrate with  $\frac{N}{10}$  Alkali - this latter procedure facilitates observing the endpoint.

It is necessary to conduct a blank determination on 50 m.l. of water, using exactly the same quantities of reagents, indicators and procedure as for the spirit, This blank will make any correction necessary which arises from impurities in the reagents, or action of the alkali on the glass of the refluxing flask.

1 m.l. of  $\frac{N}{10}$  alkali = .0088 grms ester as ethylacetate.

ALDEHYDES AND FURFURAL.

The estimation of aldehydes in spirit is of the utmost importance, as they constitute, together with the higher alcohols, the major impurities present.

Aldehydes exist probably for the most part as acetaldehyde -  $\text{CH}_3\text{CHO}$  - and have their origin in the oxidation of corresponding alcohols. Furfural which characterises all potable spirit, is absent in highly rectified spirit, or, if present, it is only in relatively small proportion, and owes its presence to the action of heat on cellulose. The proportion of aldehydes in spirit, however, of the  $\text{C}_n\text{H}_{2n}\text{O}$  series is infinitely greater than that of furfural, and in the estimation of aldehydes by the colorimetric processes described later, the furfural may be disregarded.

COLOR REAGENT.

As regards the preparation of a fuchsin reagent to be used colorimetrically for aldehyde determination the observations of various authors are noted.

Allen<sup>(8)</sup> states that the presence of much mineral acid greatly reduces the sensitivity of the reagent. Wejciechowska - Struszyuska<sup>(9)</sup> says that the intensity of the coloration given by reagents of the Schiff type with aldehydes is the greater, the greater the fuchsin content, and the smaller the SO<sub>2</sub> content of the reagent; also the sensitivity of the reagent increases with increase in the alcohol concentration, until, at very high concentrations of alcohol, the reaction is positive, even in the absence of aldehyde. Ruppin<sup>(10)</sup> remarks that colors obtained in the fuchsin-aldehyde determination, should not be matched in a colorimeter, since different degrees of color are not comparable.

These observations were confirmed and the following method for preparing the fuchsin reagent is recommended.

Dissolve 0.10 grms fuchsin in 60 m.l. of warm water and cool. Separately dissolve 1 gram. of anhydrous sodium sulphite in 10 m.l. of cold water. Mix the two solutions, add 1 m.l. of strong HCL, shake thoroughly and allow to stand overnight, then dilute to 500 m.l.



The reagent decomposes slowly, as shown by pink coloration, but will keep satisfactorily if stored away from bright light and at a low temperature.

Several reagents were made up by this method, using different samples of basic rosaniline and fuchsin supplied by chemical supply houses, and it was found that some samples were quite unsuitable for the colorimetric determinations as the solutions were brown or yellowish brown and could not be entirely bleached. However, it was found that the recommendation of Crocker <sup>(11)</sup> to use large crystals of basic rosaniline, this being the most sensitive, and the sulphite fuchsin solution being more stable than when finer divided fuchsin is used gave satisfactory results.

#### ALCOHOL.

The accuracy of aldehyde estimations colorimetrically, depend on the preparation of pure alcohol, which is used in the preparation of all standard solutions, and for the purpose of making up solutions to a definite volume, and it must be free from aldehyde and furfural.

Mann and Stacey <sup>(12)</sup> using a good quality spirit, found furfural was readily removed, but for complete removal of the aldehydes the use of aniline phosphate and Hewitts reagent were alone quite insufficient. But by very careful fractionation of the spirit they obtained a sample in which very little color was produced by the fuchsin reagent, and on redistilling this improved spirit with about 10 grms/litre of Hewitt's reagent, obtained Alcohol "Practically free from aldehyde."

Cross & Swain <sup>(13)</sup> followed the method used by the U.S. Bureau of Chemistry <sup>(14)</sup> and distilled alcohol after treatment with m-phenylenediamine hydrochloride, and the distillate was again distilled over lime, but this was found to be wasteful and tedious. A modified method was then resorted to in which the aldehydes were first polymerised with caustic soda, 0.5 gm of silver sulphate per litre was added, and refluxed for several hours. On distilling this alcohol, it was found that the last half of the distillate gave no test for aldehyde.

This difficulty of preparing aldehyde free alcohol is greater than appears to be admitted by Vasey <sup>(5)</sup> who procured rectified spirits of wine which needed "no preliminary purification", and it is interesting, in this connection, to note that in certain investigations of spirit, made under the direction of the A.O.A.C. in 1903 <sup>(15)</sup> one chemist was unable to complete the prescribed work "owing to the impossibility of obtaining aldehyde-free spirit."

In the present investigation, it was similarly found that when using 'B.P. Alcohol', 'absolute alcohol', '2% methylated alcohol', obtained from chemical supply houses, and ordinary fertifying spirit from the R.A.C. bond store, it was impossible to produce aldehyde free alcohol by the modified method of Cross and Swain, the method as directed by the A.O.A.C. <sup>(16)</sup> or by fractionally distilling spirit using a 4:1 reflux ration and collecting separate fractions.

In each case, the spirit when treated with Schniffs reagent, before and after treatment, recorded but a slight decrease in intensity of color, instead of a marked decrease as expected - Table 1 This indicated that instead of removing the aldehydes a constituent was present which, being uninfluenced by the caustic soda and phenylenediamine, or by the silver sulphate, was being carried over into the final distillate, and was recording as aldehyde by its reaction with the fuchsin - bisulphite.

TABLE 1.

Depth of color measured in a colorimeter after 15 mins.

	<u>Depth in cms.</u>
Untreated 2% methylated	40
1st 100 m.l. of distillate	43
2nd " " " "	49½
3rd " " " "	50
4th " " " "	50 Standard
5th " " " "	49
6th " " " "	46
last 100 m.l. of distillate.	42

The depth of color of the standard being approximately 4.4 red + .6 blue viewed through a depth of 2.5 cms Lovibond scale.

This constituent was thought to be acetal, and the method previously conducted, as directed by the A.O.A.C. was modified, by

first refluxing the alcohol with conc. H<sub>2</sub>SO<sub>4</sub> 5 m.l. per litre, the condenser was held at approximately 32<sup>00</sup><sup>2 4</sup> and a current of air was drawn through the apparatus - this modification was adopted with a view to hydrolysing the acetal to aldehyde and alcohol, then drawing off the aldehyde, which boils at 21<sup>00</sup>, with air, On completing the preparation and testing fractions of the final distillate with fuchsin reagent, it was shown that the aldehyde content of the intermediate distillate was little improved from the original spirit

before treatment, <sup>Table 2</sup> This treatment will be referred to as Mehted 1.

TABLE 2.

Depth of color measured in a colorimeter after 15 mins. Depth in cms. Figs. from Table

	Depth in cms.	Figs. from Table
Untreated 2% methylated	34	40
1st 100 m.l. of distillate	41	43
2nd " "	48	49½
3rd " "	50	50
4th " "	50 Standard	50
5th " "	49	49
6th " "	48	46
last 100 m.l. of distillate	45	42

The depth of color, as before, of the standard being approximately, 4.4 red + .6 blue viewed through a depth of 2.5 cms. Lovibond scale.

Further investigation using a spirit sample, which was especially drawn for the purpose, from a spirit distillation at the R.A.C. distillery, gave better results. This spirit before treatment, when compared with the 2% methylated spirit, previously used, tested with fuchsin reagent.

	Depth in cms.	Intensity of color
2% methylated	50	1
SVR ex distillation	35	1.43

the latter spirit when viewed in the Lovibond Tintometer using 2.5 cell gave 12 red + 1 blue approximately.

1500 m.l. of this spirit was then treated with 50 m.l. of 20% H<sub>2</sub>SO<sub>4</sub> and immediately distilled, the distillate being collected in 50 m.l. of 20% N<sup>2 4</sup>OH and continued until less than 100 m.l. remained.

The distillate in the N<sup>a</sup><sub>a</sub>OH was thoroughly shaken and immediately

distilled, the distillate collected until all the alcohol had passed over, shown by the presence of water vapour in the flask. 3 grs. of metaphenylenediamine per litre added and allowed to stand 10 days, or alternatively the spirit could have been refluxed on a waterbath for 5-6 hours. It was then distilled rejecting the first 100 ml. and the last 200 ml. of distillate.

Ordinary 2 litre Florence flasks and inland revenue condensers were used throughout the operations. This treatment will be referred to as method 2. This treatment was again repeated in detail on the final distillate, and results tabulated for comparison.

TABLE 3.

Depth of color measured in a colorimeter after 15 mins treatment with fuchsin reagent.

	<u>Depth cm.</u>	<u>Intensity</u>
1a. Untreated commercial fortifying spirit	1.76	28
b. Same spirit treated Method 1	15	3.3
2a. Untreated 2% methylated	34	1.5
b. Same treated Method 1	43	1
3a. Untreated S.V.R. ex distillation	23	2.2
b. Treated as Method 2	49	1
c. Treatment repeated Method 2	50 Standard	1

The depth of color of the standard chosen being approximately 4.4 red and .6 blue, in 2.5 cm. cell, Lovibond scale. These figures indicate the difficulty experienced in producing aldehyde-free alcohol, however the less the amount of impurity in the untreated spirit the better the final result as shown by 1a/ and 3a/ compared with their corresponding spirits after treatment. Further treatment of this distillate does not reduce the impurity significantly enough to warrant the treatment, compare 3b/ and 3c/.

On the foregoing figures, it is recommended to follow the treatment of method 2/, and to use a sample of spirit which does not produce more color than approximately 12 red + 1 blue when viewed through a 2.5 cm. cell Lovibond scale. Although this spirit, after treatment is not "aldehyde-free" it is suggested to carry out an experiment adding definite amounts of aldehyde to this spirit as directed by the A.O.A.C. (16). This will indicate whether the additions can be measured colorimetrically, and if so the color produced by this standard can be allowed for in further determinations.

APENDIX.

1. Sensitivity of Schiff's reagent, made up to the directions of -
  1. Elvove - Simmonds "Alcohol" page 187.
  2. Wang - British Chemical Abstracts 1932 A page 763.
  3. Analar Standards page 283 1934.
  4. Excess fuchsin and SO<sub>2</sub> 1 grm fuchsin / litre SO<sub>2</sub> bubbled in till colorless.
  5. Excess SO<sub>2</sub> 1/2 grm fuchsin / litre
  6. Excess fuchsin (prepared as A.O.A.C.) 10 grms. H<sub>2</sub>SO<sub>3</sub> sol. / litre
  7. Excess fuchsin (prepared as A.O.A.C.) 1 grm. fuchsin / litre.
  8. Excess fuchsin (prepared as A.O.A.C.) 10 grms. H<sub>2</sub>SO<sub>3</sub> solu. / litre
  9. A.O.A.C. No. 1 - Methods of Analysis page 144. 1930
  10. A.O.A.C. No. 2 - same as 7.
  11. SO<sub>2</sub> bubbled in, and excess removed by boiling + 1/2 grm. fuchsin/litre
  12. Churchward - preparation given under "Aldehydes".

Reagent

	Depth of color in cms.		
	Spirit untreated	Addition of Aldehyde	
		2 grms/litre	4 grms/litre
1.	25	27	11
2.	20	19	20
3.	17	16	16
4.	Nil	Nil	Nil
5.	355	430	155
6.	275	134	84
7.	85	73	54
8.	73	59 Standard	50
9.	81	66	40
10.	79	63	52

The depth of color of the standard being approximately 6.5 red and 1 blue when viewed through a depth of 2.5 cms in the Lovibond Tuitometer.

The conclusions to be drawn from this experiment.

Reagent: 1. The presence of much mineral acid (1%) produces too much depth of color in the undosed alcohol and hence small additions of aldehyde become difficult to detect.

2. The reagent prepared as directed by Wang is not colorless and the small additions of aldehyde could not be measured.

3. Similarly as with No. 1 and the presence of excess SO<sub>2</sub> render this reagent unsuitable.

4. Excess SO<sub>2</sub> will form the "bisulphite compound" with the added aldehyde, without the latter influencing the fuchsin.

5. Same as No. 4 even though the difference was measurable, the result was not indicative of the additions.

6. Excess fuchsin necessitated increasing the dosage of

H<sub>2</sub>SO<sub>3</sub> (saturated solution) to decolorise the reagent, and yet this reagent gave the best range of color with the addition of aldehyde.

7 & 8. These reagents, even though prepared at the same time and to the same directions, show a variation due probably to the amount of SO<sub>2</sub> contained - this indicates the difficulty experienced in quoting standards for aldehyde-alcohol concentrations by the Lovibond Tuitometer.

9. This reagent gave the most satisfactory readings as the difference between the dosages of aldehyde was measurable with a certain degree of accuracy. However, the reagent is difficult to prepare so as to contain always the same dosage of SO<sub>2</sub>.

10. This reagent compares very favourably with Nos. 7 and 8, and also No. 9, it is easily prepared and can be made up with reasonable accuracy to a definite standard, and it is this reagent which is recommended for use in the colorimetric determination of aldehydes.

However from the figures it cannot be concluded that it is measuring the actual differences in aldehyde content, as it would be necessary to work in parts per million to verify this point.

2. Aldehyde-free Alcohol.

1. Spirit untreated 2% methylated
2. Spirit 1 treated as directed by A.O.A.C. page 144.
3. Spirit 1 treated with H S.O. REFLUXED for 3 hours with a current of air, then treated as Spirit 2.
4. Spirit 3 after distilling off Na OH without treatment with metaphenylenediamine.

Reagent.	Intensity of color.				
	Spirit	1	2	3	4
1. $\frac{1}{2}$ gm. fuchsin/litre SO <sub>2</sub> bubbled in and excess removed by boiling.		30	32	34	20
2. As AOAC		<u>120</u> standard	163	173	
3. $\frac{1}{2}$ gm Fuchsin/litre SO <sub>2</sub> bubbled in till nearly colorless, then allowed to stand (slight excess of SO <sub>2</sub> , but excess not measurable.)		50	53	54	30

The depth of color of the standard being approx. 4 red in 2.5 cm. cell, Lovibond scale.

These results show that even with different Schiff's reagents, there is very little decrease in color between the untreated and the treated spirit. The spirit used in this experiments was 2% methylated; it was then decided to measure the progressive development of color in the different fractions. of the distillate.

The spirit used for this latter test was ordinary commercial fortifying spirit.

The spirit was refluxed for 2 hours with conc H<sub>2</sub>SO<sub>4</sub> and a current of air was driven through the spirit and condenser, then through some previously treated 2% methylated spirit in a test tube held at 5 °C, with the object of collecting any aldehyde which is eliminated by this treatment, and measuring the color developed by Schiff's reagent.

After this treatment, the spirit was refluxed with 10 grms. of aluminium foil and 10 grms of NaOH per litre of alcohol, after diluting the spirit, with 5% water. This refluxing was carried out for 3 hours, then distilled, and each 100 ml. were progressively collected.

The Schiff's reagents used.

1.  $\frac{1}{2}$  gram fuchsin / litre. SO<sub>2</sub> bubbled in and excess removed by boiling,
2. Prepared as in text

Spirit	Reagent 1	Reagent 2
Untreated	1.75	4
1st 100 m.l. distillate	2.5	6
2nd "	2.75	7
3rd "	3.75	8 $\frac{1}{2}$
4th "	4.5	11
5th "	6	15
6th "	15	25
last "	50	50
Untreated 2% methylated	38	42
Treated 2% " as 50 standard		50 standard
No. 3 spirit on previous page		

A better indication of the two reagents used is seen in the following table where they are both reduced to a common factor, for this purpose the two standards chosen were compared, and the table compiled taking the standard obtained with reagent 1 as the common standard.

Spirit	Depth of color		Intensity	
	Reagent 1	Reagent 2	Reagent 1	Reagent 2
Treated	2% methylated	Reagent 1	50 cms.	
"	" "	Reagent 2	30 cms.	

(cont)	<u>Depth of color</u>		<u>Intensity</u>
Untreated S.V.R.	1.75	2.4	28.5
1st 100 m.l. distillate	2.5	3.6	20.0
2nd	2.75	4.2	18.0
3rd	3.75	5.1	13.3
4th	4.5	6.6	11.1
5th	6	9	8.3
6th	15	15	3.3
Last	50	30	1.0
Untreated 2% methylated	38	25	1.3
Treated " " "	50	30	1.0
	Standard		

This indicated the unsuitability of using the method outlined for this preparation (supplied by the Customs Laboratory with the kind permission of Mr. C.R. Churchward), as although there is a progressive decrease in aldehyde content, the last of the distillate or 1/7th of the total is the only fraction which is reasonably free of aldehyde.

It also shows that the fortifying spirit which was withdrawn from the R.A.C. bondstore is unsuitable, when compared to the 2% methylated as the distillate of the latter, after treatment, comprised approximately 700 m.l. of the 1000 m.l. treated.

In the cases of "B.P. Alcohol" and "Absolute Alcohol" obtained from the chemical supply houses, when treated as the 2% methylated alcohol, very little difference in the color reactions of the distillates was found. However, a special sample of spirit withdrawn during the actual distillation of some wine at the college distillery gave, after treatment, a more satisfactory result - see Text.

In order to ascertain the stage, during the spirit run, at which it would be most suitable to draw this sample, the distillate was tested at definite intervals, the spirit being withdrawn from the "spirit-safe" and tested against a spirit referred to as "standard" for purposes of comparison.

Approx. Stgth & Time when drawn	Color intensity against No. 1 (Standard)		
	1st day	2nd day	3rd day
1 "Standard"	1.	1.	1.
2. Feints 55 <sup>OP</sup> 10 mins after commencing	1.74	2.2	2.4
3. Spirits 70 <sup>OP</sup> when changed over	1.48	1.8	1.6
4. " 72 <sup>OP</sup> 15 mins. after changing	.87	1.2	1.0



(cont)					1st day	2nd day	3rd day
5.	Spirits	72 <sup>OP</sup>	30 mins	after changing	.48	.6	.6
6.	"	73 <sup>OP</sup>	1 hour	" "	.17	.27	.13
7.	"	73 <sup>OP</sup>	2 "	" "	.094	.13	.08
8.	"	73 <sup>OP</sup>	3 "	" "	.12	.12	.07
9.	"	74 <sup>OP</sup>	4 "	" "	.14	.13	.07
10.	"		Tails	when changed over	.16	.20	.08

From these figures it was decided to withdraw the spirit sample for the laboratory after the spirit had been running for 3 hours; as it was at this stage that the spirit produced a minimum amount of color with the fuchsian reagent.

This spirit was then treated to eliminate the aldehyde impurity present - see text.

An attempt was made to measure the aldehyde present in the untreated and treated 2% methylated alcohol by the quantitative method of Jaulmes and Espézel - British chemical abstracts page 703.1935. But it was found impossible to obtain an endpoint in the iodine titration, this was due to the presence of the alcohol. Sutton-Volumetric Analysis 12th Ed. page 386 - explains that "the use of alcohol to dissolve the aldehyde, in the Ripper method" (which is conducted on the same principles) should be avoided as far as possible, as even relatively small quantities of alcohol (upwards of 5%) interfere with the iodine of starch reaction."

As this is the only quantitative method for estimating the aldehydes in spirit, the colorimetric method must, of necessity be resorted to.