5-1916

The Chemistry of Selected Food Stuffs and Condiments

Leslie F. Rutledge

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The Chemistry of Selected Food Stuffs and Condiments.

Leslie F. Rutledge.
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TABLE OF CONTENTS.

Food in Relation to Human Life .......................................................... 1.
Composition.
Sources.

Analysis of Milk:
Specific Gravity ............................................................... 5.
Determination of Fat ......................................................... 5.
Determination of Lactose ................................................... 6.
Separation of Casein and Albumin ...................... 7.
Determination of Total Protein ............... 8.
Determination of Total Solids .................. 9.
Detection of Preservatives .......................... 10.

Analysis of Butter:
Index of Refraction .................................................... 11.
Spoon or Foam Test .................................................... 11.

Analysis of Flour and Bread:
Determination of Moisture ............................................. 12.
Determination of Dextrose ............................................ 12.
Determination of Dextrin and Starch ........... 13.

Analysis of Wine:
Specific Gravity ............................................................. 14.
Determination of Alcohol .............................................. 15.
Determination of Extract ............................................. 15.
Determination of Ash .................................................. 16.
Determination of Free Acids .............................. 16.
Determination of Volatile Acids ............... 16.
Determination of Fixed Acids ...................... 17.
Determination of Alcohol in Vanilla .......... 17.
Before taking up the analytical methods employed in the work done in the laboratory, it seems fitting that a few words should be said regarding the nature of the food problem. Life itself is conditioned on the food supply and wholesome food is a necessity for productive life. Man can and does exist on very unsuitable, even more or less poisonous food, but it is merely existence and not effective life. To be well and to be able to do a day's work is man's birthright. Nevertheless, a too large proportion of the American people sell this most valuable possession for a mess of pottage which pleases the palate for three minutes and weighs the digestive organs for three hours. With the products of the world exposed in our markets, the restraints of a restricted choice, as well as inherited instincts or traditions lose their force. The buyer, unless he has actual knowledge to guide him, is swayed by the caprices of the moment or the conditions of his purse, and often fails to secure adequate return in nutritive value for the money paid. The fact that so much manipulated material is put upon the market renders this choice of food doubly difficult, since the appearance of the original article is often entirely lost, and to the city-bred buyers even the natural products convey little idea of their money value. It is now even more necessary that an elementary knowledge of the proximate composition and food value of the more common edible substances should be recognized as an essential part of education.

The chemical elements which enter into the composition of the body are determined by an analysis of the various organs and tissues. The combinations of those elements that are suitable
for food are discovered by determining those present in mother's milk and in food stuffs which experience has proved to furnish perfect nutrition. From these studies it is apparent that about fifteen chemical elements are constant constituents of the human body; that about a thousand natural products are known to have food value; that of these, one hundred are of world-wide importance, and that ten of these form nine tenths of the food of the world. The composition of food, as shown by chemical analysis, is not, however, the only factor that must be known to determine its food value. The digestibility of the material must be taken into account as well. We live not upon what we eat, but upon what we digest.

While the foodstuffs present great variety, the food principles may be grouped under four headings; viz., nitrogenous substances or proteids, fats, carbohydrates, and mineral salts. The protein or nitrogenous portion of the food forms tissues, such as muscle, sinew, and fat, and furnishes energy in the form of heat and muscular strength; the fats build up fatty tissues but not muscle, and supply heat; the carbohydrates are changed into fats and supply heat. Another important use of the nutrients is to protect each other from being used in the body. The carbohydrates, especially, in this way protect the protein, including muscle, etc., from consumption.

The composition of cooked foods is in general not the same as the raw material on account of chemical and physical changes brought about by the heat employed in the cooking process. The total nutrients, calculated on a water-free basis, may be practically the same, but the structure is quite different. As food is ordinarily prepared, about ten per cent must be deducted for indigestibility
in a customary mixed diet, and about ten per cent more for the refuse or waste of food as purchased, so that of the total pounds of meat, vegetables, and groceries some twenty per cent is of no final service to the body.

The most serious aspect of the food question is that the taking of it is voluntary, not, like air, a necessity beyond control, and that the most fantastic ideas are allowed to rule. The day laborer is in little danger, since his food demand is made strong by out-of-door exercise; but the student who shuts himself up in hot, close rooms, and who does not look upon food as his capital, but only as a disagreeable task or an amusement, is in great danger, as is he who having heard that one can live on a few cents a day, proceeds to try it without knowledge, and suffers a loss of efficiency for years or for all his life.

The foods which furnish the greatest nutrition for the least money are such materials as corn meal, wheat flour, milk, beans, cheese and sugar. The expensive cuts of meat, high-priced breakfast cereals and the like, add but little to the nutritive value but greatly increase the cost of living. Incorrect ideas in regard to food values, and prejudice inherited or acquired against certain foods, have too often resulted in excluding wholesome and nutritious articles from the dietary and decreasing thereby the efficiency of the human machine. The chief dangers in food are from wrong proportions of proteid, fats, and carbohydrates, from fermentable and irritating decompositions, from bad methods of cooking and unsuitable combinations, from transmission of micro-organisms either by exposure to dust or by contact with hands or vessels, to a favorable medium for the growth of pathogenic
germs, from unsuitable food scientifically disguised. From this hasty survey it will be seen how little danger to health is incurred if only reasonable care is taken and if the always doubtful articles are avoided.

In the discussion of the methods employed for the examination of food-materials, only a few typical substances have been considered, and the processes used are such as to bring into prominence the scientific aspect rather than the technical detail of the subject.

Both on account of its importance as a food-material and on account of its availability for the various tests, milk was chosen as a type of animal food. The analysis of milk included determinations of specific gravity, total solids, ash, proteids and sugar, the separation of casein and albumin and the detection of preservatives.

The nature and composition of the various fats and oils were obtained by the examination of butter and oleomargarine.

Wheat flour and bread were taken as typical of vegetable foods. The examinations made of this class included the determination of moisture, ash, starch, dextrose and dextrin.

The results of fermentation were illustrated by the determination of alcohol in sherry wine and vanilla extract. The determination of the relative proportion of volatile and fixed acids in sherry wine were also made.

All substances for examination, except the wine, were obtained from the Domestic Department of Ursinus College. Following is the data obtained from the work done in the Chemical Laboratory of Ursinus College under the direction and supervision of Dr. Matthew
Beardwood. The text-book used was Woodman and Norton's Air, Water and Food.

Milk is a food material of somewhat complex and variable composition but can be described as essentially an aqueous solution of milk-sugar, mineral salts and partially dissolved casein. In approximate figures the average percentage composition of milk may be stated:

<table>
<thead>
<tr>
<th>Component</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids</td>
<td>12.8</td>
</tr>
<tr>
<td>Fat</td>
<td>3.8</td>
</tr>
<tr>
<td>Protein</td>
<td>3.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.7</td>
</tr>
<tr>
<td>Milk Sugar</td>
<td>4.7</td>
</tr>
<tr>
<td>Solids not fat</td>
<td>9.0</td>
</tr>
</tbody>
</table>

However there may be in normal milk decided variations from these figures due to environment or to racial influences.

The first determination made was that of the Specific Gravity of Milk by means of the lactometer; the temperature of the milk was first taken as the Sp. Gr. varies inversely with the temperature.

Temp. of milk —— 12.2 degrees Cent.

Sp. Gr. ——— 1.031

The lactometer reading is of value in rapid analysis of milk for calculating the solids in connection with the Babcock method of fat determination, which was the next determination made.

17.6 C.C. of milk were poured into each of the graduated test bottles belonging to the Babcock apparatus. Then, to each bottle were added 17.5 C.C. of concentrated sulphuric acid. After the acid had been added the bottles were placed in opposite pockets of the centrifuge and whirled for five minutes at a speed of about 800 revolutions per minute. The bottles were then removed and hot water added up to the neck of the bottles and they were again whirled for one minute.
Hot water was then added until the fat rose nearly to the top of the graduation and again the bottles were whirled for one minute. The percentage of fat was then read from the graduations on the bottles, the result being 3.7%.

Methods based on centrifugal separation of fat, of which the Babcock method is the pioneer, are by far the most rapid and convenient for general use. They have practically replaced the more tedious extraction methods and are universally employed in creameries and milk depots.

Another important constituent of milk is milk-sugar or lactose. This was determined by its reducing action on Fehling's solution; the method of Munsen and Walker being used.

25 C.C. of milk were put into a 500 C.C. flask. To this were added 400 C.C. of water, 10 C.C. of copper sulphate solution of the same strength as that used in Fehling's solution, (69.28 gms. of Cu SO₄ per liter) 35 C.C. of tenth normal sodium hydroxide and the solution made up to 500 C.C. with water, mixed thoroughly and filtered through a dry filter.

In another beaker were mixed 25 C.C. of the Fehling's copper sulphate solution and 25 C.C. of alkaline tartrate solution, (346 gms. of crystallized potassium-sodium tartrate, dissolved in hot water and after cooling, mixed with 142 gms. of caustic soda also dissolved in water and the mixture made up to one liter). To this were added 50 C.C. of the milk-sugar solution, prepared as above, the beaker covered with a watch glass and heated on a wire gauze. The flame was so regulated that the solution began to boil in four minutes and the boiling was continued for exactly two minutes. The solution was immediately filtered through asbestos in a weighed Gooch crucible and the
precipitate washed with hot water until free from alkali. It was then washed with 10 C.C. of alcohol and finally with 10 C.C. of ether. The crucible was then dried for thirty minutes in an oven at 100 degrees Cent. and weighed. The milligrams of lactose corresponding to the weight of cuprous oxide were found from a table in the text-book.

Weight of crucible after filtering——14.435 gms.  
" " " " " " ———14.252 " "  
.183 gms. $\text{Cu}_2\text{O} = 124.3\text{mmgs. of lactose.}$

In the 50 C.C. of solution used there were 2.5 C.C. of milk.  
$124.3\text{ mmgs. of lactose in 2.5 C.C. of milk.}$  
$\frac{49720}{40} = 1243\text{ mmgs. of lactose in 100 C.C.}$

Sp.Gr. of milk=1.031

$4.9720 \times 1.031 = 4.8\%$ lactose.

The general principle upon which all such methods depend is based on the fact that certain sugars, among which is lactose, have the power of reducing an alkaline solution of copper to a lower state of oxidation in which copper is separated as cuprous oxide. The amount of reduction of the copper salt to the cuprous oxide is affected by the rate at which the sugar solution is added, the time and degree of heating and the strength of the sugar solution; hence the necessity for taking the results from a table determined by exactly the same procedure.

Separation of Casein and Albumin:— The method employed in this determination was the volumetric method of Van Slyke and Bosworth.  

20 C.C. of milk were put into a 200 C.C. graduated flask and about 80 C.C. of water added. 1 C.C. of phenolphthalein was added as an indicator and then $\text{N/10 NaOH}$ until a faint pink color remained throughout the mixture.
To the now neutralized sample were added enough N/10 acetic acid to completely precipitate the casein. The mixture was then made up to the 200 C.C. mark with water and filtered. 100 C.C. of the filtrate were titrated with N/10 NaOH and phenolphthalein to a pink color. By subtracting the number of C.C. of N/10 NaOH from one half of the C.C. of N/10 acetic acid added, the C.C. of acid required to precipitate the casein in 10 C.C. of milk were obtained. 1 C.C. of N/10 acetic acid equals 0.11315 gms. of casein.

44 C.C. N/10 CH₃(COOH) were added.

19.5 C.C. N/10 NaOH were required to neutralise 100 C.C. of filtrate.

22 C.C. - 19.5 C.C. = 2.5 C.C. N/10 CH₃(COOH) to precipitate casein in 10 C.C. of milk.

2.5 x .11315 = .282875 gms. in 10 C.C. of milk.

10 x .282875 = 2.8% casein in sample.

The determination of "Total Protein" was made by the Kjeldhal Process. This method is based upon the decomposition of the nitrogenous material by boiling with strong sulphuric acid. The carbon and hydrogen are oxidized to carbon dioxide and water, a portion of the sulphuric acid being reduced to sulphur dioxide. The nitrogen is left as ammonium sulphate from which the ammonia is liberated by caustic potash and distilled into a known excess of standard acid.

5 gms. of milk were weighed into a Kjeldahl flask, and 10 C.C. of concentrated sulphuric acid and three drops of mercury were added. The flask was then heated gently until frothing ceased and then the heat was increased. The solution was boiled until it became almost colorless. It was then allowed to cool and a few crystals of K₂MnO₄ were added. The digestate together with 20 C.C. of potassium sulphide
were put into a distilling flask and the flask connected to a con-
denser. 50 C.C. of caustic potash were then added through a separatory
funnel and the ammonia distilled off by steam and collected in a
flask containing 25 C.C. of N/10 acetic acid. After all the ammonia
had been distilled over the collecting flask was removed and the
excess of acid was titrated with N/10 NaOH, methyl orange being used
as an indicator.

7 C.C. N/10 NaOH were required to neutralise solution.

.: 18 C.C. N/10 acetic acid were neutralised by the ammonia.

18 C.C. N/10 acid = 1.8 C.C. normal acid = 1.8 C.C. normal ammonia.
1.8 C.C. normal ammonia = 1.8 \times 0.017 = 0.0306 gms. of ammonia.

Of this 0.0306 gms. of ammonia, 0.0252 gms. are nitrogen.

\[
\text{0.0252 gms. of nitrogen in 5 gms. of milk.}
\]
\[
\text{0.5040 gms. of nitrogen in 100 gms. of milk.}
\]

To change nitrogen into protein 0.5040 was multiplied by the
factor, 6.38, the result being 3.2% protein in the milk.

Owing to the fact that the apparatus for the determination
of total solids, was not available, they had to be calculated by
formula. The fact that the constituents of milk are present in a fairly
constant ratio makes it possible to do this with sufficient accuracy
to indicate the adulteration of a sample. The following formula is
that of Hehner and Richmond.

\[
T = L/R + 1.2 F + 0.14
\]

T = Per cent of total solids.
L = Lactometer reading.
F = Fat.

\[
T = \frac{31}{4} + (1.2 \times 3.7) + 0.14
\]
\[
T = 12.33\%
\]
The preservatives most commonly employed in milk are boric acid and formaldehyde. Since the milk from the Domestic Department of the College contained no preservatives, they had to be added. To a sample of milk was added a little formaldehyde and the following examination then made.

To 10 C.C. of the sample in a porcelain dish were added 10 C.C. of HCl and one drop of ferric chloride. The dish was then heated until the contents nearly boiled. During the heating and for a few minutes after the flame was removed the contents were stirred vigorously. Then about 50 C.C. of water were added. A violet color appeared in the particles of precipitated casein, which indicated the presence of formaldehyde.

To another quantity of milk was added a little boric acid and an examination made. The milk was first made alkaline with lime water and then evaporated to dryness on a water-bath. The residue was charred over a flame. It was then digested with 20 C.C. of water and HCl added until the mixture was faintly acid to litmus paper. This was filtered and 1 C.C. of acid added in excess. A piece of turmeric paper was placed in the solution and the solution evaporated to dryness. The paper became red in color, which indicated the presence of boric acid.

Examinations of butter:— These examinations were not so much for determining the purity of the butter, but rather a comparative study of genuine butter and oleomargarine. The most important of these experiments was the one carried out with the refractometer. This was performed at Medico-Chirurgical College with a Zeiss Butter Refractometer. A specimen from the College was examined and also a
sample of oleomargarine, and the following results obtained.

For Butter:-

Temperature 40 degrees Cent.

Reading on Scale or Scale Division ------- 42.55
Index of Refraction corresponding ------- 1.4542

For Oleomargarine:-

Temperature 40 degrees Cent.

Reading on Scale or Scale Division ------- 51.28
Index of Refraction corresponding ------- 1.4602

The transformation of scale division into Index of Refraction was taken from a table found in Leach's, Food Inspection and Analysis.

The index of refraction decreases with rising temperature. The determination of the refractive index is especially valuable in the examination of butter owing to the rapidity with which the test can be made and the fact that so little of the substance is required.

Another test to distinguish between Genuine Butter and Oleomargarine, was the Spoon test or Foam test. The butter to be examined was put into a small tin dish and melted. The heat was then increased until the fat boiled briskly, stirring taking place continuously. It boiled with little noise and produced an abundance of foam which was the indication of good butter. A sample of oleomargarine was put to the same test. This boiled noisly and with much sputtering and produced very little foam.

This method is of value for giving a quick decision regarding a sample, and is especially useful for the detection of renovated butter. The crackling and sputtering of the fat in the case of oleomargarine are due to the fact that in the process of manufacture
the melted fat is sprayed into ice-water, and the cooled particles enclose some water.

The next substances examined were flour and bread as samples of vegetable foods. Whole wheat flour was used for the determination of moisture and bread was used in the determination of dextrose, dextrin and starch.

About 2 grams of the flour were spread in a thin layer on a watch glass and dried in an oven at 100 degrees Cent. for five hours.

Weight of crystal and flour before drying — 6.154 gms.
" " " after " " 5.977 "

.177 gms. of moisture in 2 gms. of flour.

\[ \begin{array}{c}
50 \\
8.850\% \text{ moisture.}
\end{array} \]

Determination of Dextrose, Dextrin, and Starch in Bread:— A sample of bread was obtained from the College Domestic Department; this was put in water and the mixture heated almost to boiling for about an hour. It was then filtered and aliquot portions of the filtrate tested for the above constituents by Fehling’s solution.

25 C.C. of the bread extract and 50 C.C. of Fehling’s solution were put into a beaker. The beaker was covered with a watch glass and heated. The flame was so regulated that boiling began in about four minutes and continued for exactly two minutes. The solution was immediately filtered through asbestos in a Gooch crucible and the precipitate washed with hot water until free from alkali. Then it was washed with 10 C.C. of alcohol and finally with 10 C.C. of ether. The crucible was then dried for thirty minutes in an oven at a temp. of 100 degrees Cent. and weighed. The results were calculated as dextrose,
the amount corresponding to the weight of cuprous oxide being taken from a table in the text-book.

25 C.C. of bread extract:--

Weight of crucible after filtering ---- 13.840 gms.
" " before " ---- 13.783 gms.

.057 gms. Cu₂O = 57mmgs. = 24.34mmgs. of dextrose.

Another portion of the extract was hydrolized by means of dilute HCl in order to convert the starch and dextrin into sugar. The hydrolized solution was then put through the same process as was carried on in the above experiment. The results gave the amount of total sugar. The difference between the results of the first determination and those of the second, gave the amount of sugar from starch and dextrin.

Weight of crucible after filtering ---- 16.557 gms.
" " before " ---- 13.764 "

2.793 gms. Cu₂O = 2793mmgs. = 1255.88mmgs. of dextrose:

1255.88 - 24.34 = 1231.54mmgs. dextrose from starch and dextrin.

In another portion of the extract the starch was precipitated with Ba(OH)₂ and the solution filtered. The filtrate was hydrolized by dilute HCl, thus converting the dextrin into sugar. The sugar was then determined by Fehling's solution. The difference between the results from the first determination and those of this determination was the amount of dextrin in terms of dextrose. Then by subtracting the amount of dextrin plus the dextrose from the first determination, the amount of starch in terms of dextrose was obtained.
Weight of crucible after filtering --- 14.070 gms.
" " before " --- 13.821 "
\[ \frac{14.070 - 13.821}{0.249} = 112.3 \text{ mmgs. of dextrose} \]

112.3 - 24.34 = 87.96 mmgs. of dextrin in terms of dextrose.
1231.54 - 87.96 = 1143.58 mmgs. of starch in terms of dextrose.

The examinations of fermented liquors were made on sherry wine and vanilla extract. The object of the wine analysis was to determine whether it was pure and unadulterated. The determinations made in judging the purity of the wine were alcohol, extract, ash, total, free and volatile acids. The analytical methods used in these determinations were more for practice in the examination of a fermented product and are not as thorough as would be necessary to judge the genuineness of a wine.

The first determination was that of specific gravity by means of the pyknometer. This result was then checked up by Westphal’s specific gravity balance.

Temperature of wine -- 18 degrees Cent.

Weight of empty pyknometer ---- 24.875 gms.
" " pyknometer filled with wine ---- 124.207 gms.
" " " " water ---- 124.8 "

\[ \frac{124.207 - 124.8}{0.249} = 112.3 \text{ mmgs. of dextrose} \]

124.2070 - 124.8 = .995 = specific gravity of wine.

The specific gravity was then taken with the Sp.Gr.Balance and found to be .993. However, the temperature of the wine in the second trial was 20 degrees instead of 18 as in the first, and this was responsible for the difference.

In making the alcohol determination, the alcohol was first obtained free from everything but water and its amount determined by ascertaining the specific gravity of the mixture. The percentage
was then taken from a table in the text-book.

50 C.C. of the wine were measured into a 250 C.C. flask and 25 C.C. of water added. The mixture was then distilled until about 50 C.C. had been collected in the receiving flask. The specific gravity of the distillate was then taken by means of a pyknometer and found to be .983. On consulting the table it was found that the percentage of absolute alcohol by volume was 13.43. This percentage comes within the limits of normal wines. Wines are sometimes fortified to the amount of 20%, but fermentation does not yield over 14%.

In making the determination for extract a preliminary calculation was made by the use of a formula, since the method to be employed depended upon the extract content.

\[ X = 1 + d - d' \]

\( X = \text{Sp.Gr. of dealcoholized wine.} \)
\( d = \text{Sp.Gr. of the wine.} \)
\( d' = \text{Sp.Gr. of distillate obtained in determination of alcohol.} \)

\[ X = 1 + .993 - .983 = 1.01 \]

From table; 1.01 = 2.5% extract content.

Having determined approximately the extract content, the following analytical method was employed, it being the one used for all wines having an extract content less than 3 per cent.

25 C.C. of wine were evaporated, in a weighed platinum dish, to a sirupy consistency. The residue was then heated in an oven at 100 degrees Cent. for two hours and a half and cooled in a desicator overnight. It was then weighed.

\[ \text{Weight of crucible with extract} --- 24.1 \text{ gms.} \]
\[ \" \" \text{empty crucible} --- 23.5 \text{ gms.} \]
\[ .6 \text{ gms extract for 25 C.C. of wine.} \]
\[ 4 \times .6 = 2.4\% = \text{extract content.} \]
In determining the ash, the residue from the extract determination was ignited at a low red heat until the ash was white. The crucible was then cooled and weighed.

Weight of crucible containing ash --- 23.559 gms.
" " empty crucible ----------- 23.5 ___
.059 gms. of ash in 25 C.C. of wine.

4 x .059 = .236 = percentage of ash.

The amount of ash in a natural wine should average about ten per cent of the extract.

The free acids of the wine were calculated as tartaric acid:- 25 C.C. of the wine were measured into a small beaker and heated just below the boiling point, to expel the CO₂. It was then titrated with N/10 NaOH and phenolphthalein and the results calculated as tartaric acid. One C.C. of N/10 NaOH equals .0075 gms. of tartaric acid.

\[\frac{29.1 \text{ C.C.} \times \frac{1}{10} \text{NaOH}}{0.0075} = 1.21825 \text{ gms. of tartaric acid in 25 C.C. of wine} \]

\[4 \times 1.21825 = 4.87300\% \text{ free acids.} \]

The volatile acids were calculated as acetic acid: - 50 C.C. of the wine were measured into a 300 C.C. flask and distilled by steam, the flame under the wine being so regulated that the volume remained constant. Distillation was continued until 50 C.C. had been collected in the receiving flask. This was titrated with N/10 NaOH and phenolphthalein, and the results calculated as acetic acid. One C.C. N/10 NaOH equals .006 gms. of acetic acid.

\[\frac{5.8 \text{ C.C.} \times \frac{1}{10} \text{NaOH}}{0.006} = 0.9348 \text{ gms. of acetic acid in 50 C.C. of wine} \]

\[2 \times 0.9348 = 1.8696\% \text{ volatile acids.} \]
The fixed acids were found by calculating the volatile acids as tartaric acid and subtracting the result from the total tartaric acid found by direct titration.

\[
\begin{align*}
0.0075 \text{ gms. of acetic acid} &= 1 \text{ C.C. N/10 NaOH.} \\
5.8 \text{ C.C. N/10 NaOH.} \\
0.04350 \text{ volatile acids as tartaric acid.} \\
0.21825 \text{ gms. of total tartaric acid.} \\
0.04350 \quad " \quad " \quad " \quad \text{volatile acids as tartaric acid.} \\
0.17475 \text{ gms. of fixed acids.}
\end{align*}
\]

\[
0.17475 \text{ gms. of fixed acids in 50 C.C. of wine:} \\
2 \times 0.17475 = 0.3495\% \text{ fixed acids.}
\]

The total acids in a wine vary usually between .45% and 1.5%. The volatile acids should not be over .12 to .16%, depending upon the age of the wine.

The alcohol determination in vanilla extract was performed the same as that of wine. The specific gravity of the distillate being .957. According to the table in the text-book this represents an alcohol percentage of .30.35.

THE END.