

A Study of Terpeneless Lemon
Extracts

by C. Clay Spilman

1912

Chemical Engineering senior thesis project of the
University of Kansas

S E N I O R T H E S I S .

A S T U D Y O F

T E R P E N E L E S S L E M O N E X T R A C T S .

SUBMITTED TO

THE SCHOOL OF ENGINEERING,

UNIVERSITY OF KANSAS.

MAY 27 , 1912.

R00055 38090

1208 Mississippi St.

Lawrence, Kansas.

May 27, 1912.

To the Faculty of the
School of Chemical Engineering.
University of Kansas, Lawrence, Kansas.

Sirs :-

I desire to offer the accompanying
paper for credit as a Senior Thesis, such as is required
of all applicants for a degree in the School of Engineering.

Very respectfully submitted,

C. Clay Spilman.

TERPENELESS LEMON EXTRACTS.

There are two extracts which have the flavor of lemon and which have approximately the same citral content. They are Lemon Extract and Terpeneless Lemon Extract. These extracts are both standardized by the government.

Lemon extract, so labeled, which is placed on the market must, in order to comply with the Kansas Pure Food Law, contain five (5) per cent. by volume of oil of lemon. In order to contain this amount of lemon oil in the extract it is necessary to dissolve the oil in about eighty (80) per cent. ethyl alcohol.

Ethyl alcohol is very expensive so in order to make cheaper extracts the manufacturers have placed on the market an extract made with about fifty (50) per cent. alcohol. This is called a Terpeneless Lemon Extract for the reason that the terpenes in the lemon oil are insoluble in this strength alcohol and hence are removed mechanically from the extract. The Kansas Pure Food Law has the following regulation in regard to terpeneless lemon extracts; "Terpeneless Extract of Lemon is the flavoring extract prepared by shaking oil of lemon with dilute alcohol, U.S.P., or by dissolving terpeneless oil of lemon in dilute alcohol, U.S.P., and contains not less than two-tenths (0.2) per cent. by weight of citral derived from oil of lemon." By U.S.P.

is meant 50% alcohol.

The terpenes can be removed from lemon oil by vacuum distillation and this terpeneless oil is easily dissolved in dilute alcohol so as to obtain a standard extract. This terpeneless oil is very expensive and the vacuum distillation is not easy for a small manufacturer to handle.

It has been found by Jackson¹ that all the terpeneless lemon extracts as found on the market fall below the standard above mentioned in the per centage of citral. This fact is evidently not due to a desire to defraud but to an ignorance of the conditions which go to make a legal terpeneless lemon extract.

This thesis^{aims} to investigate the conditions which are necessary to make terpeneless lemon extracts and to find out the most economical manner of preparing a legal terpeneless extract of lemon.

In analyzing lemon extracts the criterion is the per centage of citral. In this work Hiltner's² method for the determination of citral was used on account of its rapidity and also the fair degree of accuracy which could be obtained. A copy of this method is as follows:-

METAPHENYLENE DIAMIN HYDROCHLORID SOLUTION.

Prepare a 1% solution of metaphenylene diamine

1. Kansas State Board of Health Bulletin. March 1911.
2. Bulletin No. 132, U.S. Department of Agriculture.

hydrochlorid in 50% alcohol. Decolorize by shaking with fuller's earth or animal charcoal and filter through a double filter. The solution should be bright and clear, free from suspended matter, and practically colorless. It is well to prepare only enough solution for the days work, as it darkens on standing.

ALCOHOL. For the analysis of lemon extracts 90 to 95% alcohol should be used but for terpeneless extracts alcohol of 40 to 50% strength is sufficient. Filter to remove any suspended matter. The alcohol need not be purified from aldehyde. If not practically colorless, render slightly alkaline with NaOH and distill.

APPARATUS. Use any convenient colorimeter.

MANIPULATIONS. All of the operations may be carried on at room temperature. Weigh into a 50 cc. graduated flask 25 gm. of the extract and make up to the mark with alcohol (90-95%). Stopper the flask and mix the contents thoroughly. Pipette into the colorimeter tube 2 cc. of the solution, add 10 cc. of metaphenylene diamine hydrochlorid reagent, and complete the volume to 50 cc. (or other standard volume) with alcohol. Compare at once the color with that of the standard which should be prepared at the same time, using 2 cc. of standard citral solution and 10 cc. of the metaphenylene diamine hydrochlorid reagent and making up to the standard volume with alcohol. From the result of this first determination calculate approximately the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample

under determination, then repeat the determination.

The metaphenylene diamine hydrochlorid solution was not treated with fuller's earth or animal charcoal because it has been found¹ that this treatment sometimes augments the color rather than reduces it. The salt was weighed within a hundredth of a gram, dissolved in 50% alcohol in a graduated flask and the solution then filtered.

A Schreiner colorimeter was used. The tubes used were calibrated for 50 cc. On the first tube the distance from the bottom to the 50 cc. mark was divided into 100 parts and on the second into 50 parts. The unknown extract was placed in the first tube and the standard citral solution was placed in the second. The standard was set at the 50 cc. mark and the unknown tube varied. When the colors were equal and the unknown tube read 100 then the strengths of the solutions were said to be equal. This reading is not percentage of citral but is an arbitrary number. The method of analysis above given was followed exactly except for the following changes. It was found that when 10 cc. of the one per cent. metaphenylene diamine hydrochlorid were used that the volume in the tubes was not large enough to permit reading through a large enough range. This difficulty

1. Jackson, Mory, Bulletin 132, U.S. Dept. Agri. Page 170.

was overcome by using 20 cc. of a .5% solution. The procedure for the analysis of an extract was as follows. The solutions were placed in the tubes which were then brought to the 50 cc. mark with alcohol, taking care that this alcohol was stronger than the alcohol in which the standard or extract was made. The 20 cc. of .5% metaphenylene diamin hydrochlorid solution was then added using a 20 cc. pipette. The tubes were then mixed by covering the open end by the palm of the hand and inverting twice. The tubes were then placed in the colorimeter and several minutes were allowed to elapse before making a reading in order to allow the air in the tubes to escape.

Great trouble was experienced in obtaining sufficient alcohol to carry on the work. The University did not receive any alcohol during the term in which this investigation was carried out and the delay which this occasioned is given as the reason why more data was not obtained. The alcohol was recovered as soon as used. A still was set up consisting of two electric hot plates upon which were placed two one liter German flasks. These two flasks were connected to the same small Liebig condenser.

It is not stated in the method of citral analysis whether both tubes shall be made up ^{with} and contain the same strength of alcohol. The alcoholic strength of the metaphenylene diamin hydrochlorid solution is stated and it is also stated that the alcohol used in the tubes must be as strong as that in which the extract or standard

were made in but it is not stated whether both tubes need to be made up with the same strength. This was the first Point that was investigated.

A standard of .1 gm. of citral in 100 cc. of 92% alcohol was made up. Two cubic centimeters of this standard were placed in each tube and the tubes brought to the mark with different strengths of alcohol. The standard tube was set at 50 for the reasons above mentioned and the other tube compared with it.

In all the tables given in this work the following is to be noted. The strength of alcohol mentioned is not the real alcoholic strength of the solutions in the tubes but it is the strength of the alcohol which was used in completing the volume to 50 cc. Also the 100 stated on the standard tube is really 50 but since it is equivalent to 100 on the unknown tube it is so stated.

T A B L E 1.

(a) 3-8-12.

(b) 3-8-12.

standard tube.	Unknown tube	Standard tube.	Unknown tube
86% alcohol	70% alcohol.	86% alcohol.	40% alcohol
2cc.standard.	2cc.standard.	2cc.standard.	2cc.standard
100	109	100	112
	102		108
	110		115
	100		110
	106		114
	<u>527</u>		<u>559</u>
	av.105.4		av.111.8

(c) 3-8-12.

(d) 3-8-12.

Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
86% alcohol.	20% alcohol.	20% alcohol.	20% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	120	100	103
	112		96
	118		99
	117		97
	120		101
	<u>587</u>		<u>496</u>
	av. 117.4		av. 99.2

This shows a decrease in the strength of the color of the unknown solution as the alcoholic strength decreases. (d) was run to see if a check could be obtained with equal strength in both tubes. A decrease from 70% to 40% gave a difference of 6.4; while a decrease from 40% to 20% gave a difference of 5.6.

The first bottle of metaphenylene diamine hydrochlorid which was used was ~~su~~ rather old and gave a solution which was sufficiently colored to enable one to read without having any citral present. To see the result without citral being present the following data was obtained.

T A B L E 2.

(a) 3-9-12.		(b) 3-9-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
94.5I% alcohol	70% alcohol.	94.5I% alcohol	50% alcohol.
No citral	no citral	no citral	no citral.
100	94	100	90.
	92		94
	91		93
	93		96
	90		98
	<u>460</u>		<u>471</u>
	av. 92		av. 94.2
(c) 3-9-12.		(d) 3-9-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
94.5I% alcohol	40% alcohol.	94.5I% alcohol	20% alcohol.
no citral.	no citral.	no citral.	no citral.
100	109	100	78
	101		72
	113		71
	108		72
	109		80
	<u>540</u>		<u>373</u>
	av. 108		av. 74.6
(e) 3-9-12.			
Standard tube.	Unknown tube.		
94.5I% alcohol	94.5I% alcohol.		
no citral.	no citral.		
100	103		
	102		
	100		
	102		
	102		
	<u>509</u>		
	av. 101.8		

Table 2 shows a variation in the same direction as table 1 with the exception of (d)2. This result is in the wrong direction and it is doubtful whether any weight should be given to it.

The following results were obtained with 2 cc. of standard citral in each tube and varying per cents of alcohol.

T A B L E 3.

(a) 3-9-12.		(b) 3-9-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
94.51% alcohol	50% alcohol.	94.51% alcohol	40% alcohol.
2 cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	118	100	126
	114		124
	116		127
	113		120
	<u>113</u>		<u>124</u>
	<u>574</u>		<u>621</u>
	av. 114.8		av. 124.2
(c) 3-9-12.			
Standard tube.	Unknown tube.		
94.51% alcohol	20% alcohol.		
2cc. standard.	2cc. standard.		
100	122		
	Other read-		
	ings off		
	the scale.		

This shows a weakening of color with decrease of strength of alcohol in the same direction as the previous experiments.

To see if a reading of 100 or thereabouts could be obtained when both tubes were made up with the same strength of alcohol the following experiments were made.

T A B L E 4.

(a) 3-15-12.		(b) 3-15-12.	
Standard tube.	Unknown tube.	Same as (a) but tubes	
90% alcohol.	90% alcohol.	changed in colorimeter.	
no citral.	no citral.		
100	101	100	100
	99		97
	104		106
	98		100
	99		93
	<u>501</u>		<u>496</u>
	av. 100.2		av. 99.2
(c) 3-15-12.		(d) 3-15-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
80% alcohol.	80% alcohol.	50% alcohol.	50% alcohol.
no citral.	no citral.	no citral.	no citral.
100	96	100	100
	98		104
	93		96
	94		100
	91		96
	<u>472</u>		<u>101</u>
	av. 94.4		<u>597</u>
			av. 99.5
(e) 3-15-12.		(f) 3-15-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
80% alcohol.	80% alcohol.	40% alcohol.	40% alcohol.
no citral.	no citral.	no citral.	no citral.
100	96	100	96
	97		106
	96		100
	100		102
	93		103
	100		<u>507</u>
	96		av. 101.4
	<u>678</u>		
	av. 96.8		

(g) 3-15-12.

Standard tube. Unknown tube.
 90% alcohol. 90% alcohol.
 no citral. no citral.

100	99
	99
	98
	94
	100
	96
	<u>104</u>
	<u>690</u>
	av. 98.5

(h) 3-15-12.

Standard tube. Unknown tube.
 80% alcohol. 80% alcohol.
 no citral. no citral.

100	99
	102
	97
	102
	99
	<u>499</u>
	av. 99.8

(i) 3-15-12.

Standard tube. Unknown tube.
 50% alcohol. 50% alcohol.
 no citral. no citral.

100	96
	97
	104
	106
	97
	<u>500</u>
	av. 100

(j) 3-15-12.

Standard tube. Unknown tube.
 40% alcohol. 40% alcohol.
 no citral. no citral.

100	102
	103
	95
	97
	94
	<u>491</u>
	av. 98.2

The fact that these readings did not come closer to 100 is probably due to errors of the eye but the variation is not near as large as when a different strength of alcohol is used in each tube.

A continuation of the work in Table 2 is given in Table 5.

T A B L E 5.

(a) 3-22-12.		(b) 3-22-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
90% alcohol.	80% alcohol.	90% alcohol.	50% alcohol.
no citral.	no citral.	no citral.	no citral.
100	108	100	104
	101		104
	98		102
	101		102
	<u>100</u>		<u>106</u>
	<u>508</u>		<u>518</u>
	av.101.6		av.103.6
(c) 3-22-12.		(d) 3-23-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
90% alcohol.	40% alcohol.	90% alcohol.	80% alcohol.
no citral.	no citral.	no citral.	no citral.
100	100	100	104
	108		98
	111		104
	100		106
	<u>106</u>		<u>103</u>
	<u>525</u>		<u>515</u>
	av.105		av.103

The variation obtained in Table 5 while not as large as obtained previously is still in the same direction. A new bottle of metaphenylene diamine hydrochlorid was used. There was so little color developed that no readings could be obtained.

Since no readings could be obtained with the new metaphenylene diamine solution standard citral solution was used to develop the color.

In Table 6 the solutions were made with the same strength of alcohol. 2cc. of standard were used.

T A B L E 6.

(a) 3-23-12.		(b) 3-23-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
80% alcohol.	80% alcohol.	50% alcohol.	50% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	96	100	102
	97		98
	96		116
	98		100
	95		116
	<u>482</u>		<u>532</u>
	av. 96.4		av. 106.4
(c) 3-23-12.		(d) 3-23-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
40% alcohol.	40% alcohol.	30% alcohol.	30% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	96	100	109
	90		100
	90		99
	96		103
	98		96
	<u>464</u>		<u>507</u>
	av. 92.8		av. 101.4
(e) 3-23-12.		(f) 3-23-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
80% alcohol.	80% alcohol.	50% alcohol.	50% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	96	100	97
	99		97
	102		98
	99		101
	94		94
	<u>490</u>		<u>487</u>
	av. 98		av. 97.4

(g) 3-23-12.

Standard tube. Unknown tube.

40% alcohol. 40% alcohol.

2cc. standard. 2cc. standard.

100	97
	100
	100
	98
	98
	<u>493</u>
	av. <u>98.6</u>

(h) 3-23-12.

Standard tube. Unknown tube.

30% alcohol. 30% alcohol.

2cc. standard. 2cc. standard.

100	94
	100
	106
	104
	106
	<u>510</u>
	av. <u>102</u>

(i) 3-25-12.

Standard tube. Unknown tube.

80% alcohol. 80% alcohol.

2cc. standard. 2cc. standard.

100	103
	96
	94
	95
	97
	<u>485</u>
	av. <u>97</u>

(j) 3-25-12.

Standard tube. Unknown tube.

50% alcohol. 50% alcohol.

2cc. standard. 2cc. standard.

100	103
	92
	98
	98
	103
	<u>494</u>
	av. <u>98.8</u>

(k) 3-25-12.

Standard tube. Unknown tube.

40% alcohol. 40% alcohol.

2cc. standard. 2cc. standard.

100	106
	103
	98
	93
	103
	<u>503</u>
	av. <u>100.6</u>

(l) 3-25-12.

Standard tube. Unknown tube.

80% alcohol. 80% alcohol.

2cc. standard. 2cc. standard.

100	102
	97
	100
	94
	96
	<u>489</u>
	av. <u>99.8</u>

(m) 3-25-12.

Standard tube. Unknown tube.
 50% alcohol. 50% alcohol.
 2cc. standard. 2cc. standard.

100	93
	102
	93
	98
	96
	<u>482</u>
	av. 96.4

(n) 3-25-12.

Standard tube. Unknown tube.
 40% alcohol. 40% alcohol.
 2cc. standard. 2cc. standard.

100	91
	94
	95
	97
	<u>101</u>
	<u>478</u>
	av. 95.6

(o) 3-25-12.

Standard tube. Unknown tube.
 30% alcohol. 30% alcohol.
 2cc. standard. 2cc. standard.

100	96
	96
	98
	101
	96
	<u>487</u>
	av. 97.4

(p) 3-25-12.

Standard tube. Unknown tube.
 80% alcohol. 80% alcohol.
 2cc. standard. 2cc. standard.

100	100
	96
	93
	99
	97
	<u>485</u>
	av. 97

(q) 3-25-12.

Standard tube. Unknown tube.
 50% alcohol. 50% alcohol.
 2cc. standard. 2cc. standard.

100	97
	97
	94
	95
	90
	<u>473</u>
	av. 94.6

(r) 3-25-12.

Standard tube. Unknown tube.
 40% alcohol. 40% alcohol.
 2cc. standard. 2cc. standard.

100	98
	100
	91
	93
	93
	<u>475</u>
	av. 95.

The results given in Table 6 are not very close to 100 but the error is evidently a personal one due very probably to the eyes.

In Table 7 the solutions were brought to the mark with different strengths of alcohol and they contained 2cc. of standard citral solution.

T A B L E 7.

(a) 3-28-12.		(b) 3-28-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
50% alcohol.	80% alcohol.	50% alcohol.	50% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	66	100	102
	70		98
	67		94
	65		95
	64		93
	<u>332</u>		<u>482</u>
	av. 66.4		av. 96.4
(c) 3-28-12.		(d) 3-28-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
50% alcohol.	40% alcohol.	50% alcohol.	30% alcohol.
2cc. standard.	2cc. standard.	2cc. standard.	2cc. standard.
100	104	100	116
	98		110
	106		120
	100		110
	102		118
	<u>510</u>		<u>574</u>
	av. 102		av. 114.8

(e) 3-28-12.

Standard tube. Unknown tube.
 50% alcohol. 80% alcohol.
 2cc. standard. 2cc. standard.

100	74
	65
	72
	74
	66
	<u>351</u>
	av. 70.2

(f) 3-28-12.

Standard tube. Unknown tube.
 50% alcohol. 50% alcohol.
 2cc. standard. 2cc. standard.

100	97
	96
	97
	102
	98
	<u>490</u>
	av. 98

(g) 3-28-12.

Standard tube. Unknown tube.
 50% alcohol. 40% alcohol.
 2cc. standard. 2cc. standard.

100	108
	106
	106
	104
	105
	<u>529</u>
	av. 105.8

(h) 3-28-12.

Standard tube. Unknown tube.
 50% alcohol. 30% alcohol.
 2cc. standard. 2cc. standard.

100	113
	110
	114
	110
	114
	<u>561</u>
	av. 112.2

In Table 7 the same thing is found as in Tables 1-2-3 and 5 namely that the strength of the color decreases as the strength of the alcohol decreases.

To make sure that the above was a correct conclusion the writer was assisted by Jackson in making some readings. The procedure was as follows. The writer made up the tubes and read them. Then Jackson, who had no knowledge of the contents of the tubes, read them and recorded his results on a separate paper. In several instances, as is noted, the writer read the tubes before

1. Ibid.

and then after Jackson's reading. The following results were obtained.

T A B L E 8.

Spilman.		Jackson.
(a) 3-29-12.		
Standard tube.	Unknown tube.	
80% alcohol.	80% alcohol.	
2cc. standard.	2cc. standard.	95
100	94	94
	96	97
	90	94
	92	94
	90	92
	<u>462</u>	<u>660</u>
	av. <u>92.4</u>	av. <u>94.3</u>
(b) 3-29-12.		
Standard tube.	Unknown tube.	
80% alcohol.	80% alcohol.	
2cc. standard.	2cc. standard.	97
100	96	98
	94	103
	94	101
	93	97
	92	103
	<u>471</u>	100
	av. <u>94.2</u>	<u>102</u>
		<u>801</u>
		av. <u>100.1</u>
(c) 3-29-12.		
Standard tube.	Unknown tube.	
50% alcohol.	50% alcohol.	
2cc. standard.	2cc. standard.	
100	92	98
	91	98
	95	99
	93	102
	96	<u>101</u>
	<u>467</u>	<u>498</u>
	av. <u>93.4</u>	av. <u>99.6</u>

Spilman.	Jackson.	After Jackson.
(d) 3-29-12.		
Standard tube. Unknown tube.		
40% alcohol. 40% alcohol.		
2cc. standard. 2cc. standard.		
100	98	98
	100	99
	96	95
	100	90
	92	94
	<u>486</u>	<u>476</u>
	av. <u>97.2</u>	av. <u>95.2</u>
	100	100
		99
		98
		102
		100
		<u>499</u>
		av. <u>99.8</u>

(e) 3-29-12.		
Standard tube. Unknown tube.		
80% alcohol. 50% alcohol.		
2cc. standard. 2cc. standard.		
100	78	69
	78	68
	79	72
	71	69
	74	75
	<u>380</u>	<u>353</u>
	av. <u>76</u>	av. <u>70.6</u>
	74	
	72	
	74	
	72	
	74	
	<u>366</u>	
	av. <u>73.2</u>	

(f) 3-29-12.		
Standard tube. Unknown tube.		
30% alcohol. 30% alcohol.		
2cc. standard. 2cc. standard.		
100	103	97
	98	100
	95	97
	98	98
	98	94
	<u>483</u>	<u>486</u>
	av. <u>96.6</u>	av. <u>97.2</u>
	103	
	101	
	100	
	101	
	102	
	<u>507</u>	
	av. <u>101.4</u>	

Spilman.		Jackson.	After Jackson.
(g) 3-29-12.			
Standard tube.	Unknown tube.		
30% alcohol.	50% alcohol.		
2cc. standard.	2cc. standard.	120	
		121	
100	110	117	109
	101	119	110
	114	116	111
	107	116	97
	114	116	111
	<u>546</u>	<u>825</u>	<u>538</u>
	av. 109.2	av. 118	av. 107.6

(h) 3-29-12.			
Standard tube.	Unknown tube.		
50% alcohol.	50% alcohol.		
2cc. standard.	2cc. standard.		
100	89	100	93
	88	103	93
	89	100	93
	92	99	96
	95	98	91
	<u>453</u>	<u>500</u>	<u>466</u>
	av. 90.6	av. 100	av. 93.2

(i) 3-29-12.			
Standard tube.	Unknown tube.		
40% alcohol.	40% alcohol.		
2cc. standard.	2cc. standard.		
100	101	100	99
	104	100	98
	97	98	98
	98	101	98
	98	101	95
	<u>498</u>	<u>500</u>	<u>488</u>
	av. 99.8	av. 100	av. 97.6

Spilman.		Jackson.	After Jackson.
(j) 3-29-12.			
Standard tube.	Unknown tube.		
50% alcohol.	50% alcohol.		
2cc. standard.	2cc. standard.		
100	99	104	
	95	100	
	92	105	92
	97	102	100
	94	101	94
	<u>94</u>	103	97
	<u>477</u>	104	98
	av. <u>95.4</u>	<u>719</u>	<u>481</u>
		av. <u>102.7</u>	av. <u>96.2</u>

(k) 3-29-12.			
Standard tube.	Unknown tube.		
40% alcohol,	50% alcohol,		
2cc. standard.	2cc. standard.		
100	100	109	
	101	109	
	107	114	
	106	109	
	106	104	100
	<u>106</u>	106	102
	<u>520</u>	103	98
	av. <u>104</u>	107	105
		<u>103</u>	<u>98</u>
		<u>966</u>	<u>503</u>
		av. <u>107</u>	av. <u>100.6</u>

(l) 3-29-12,			
Standard tube.	Unknown tube.		
80% alcohol.	50% alcohol.		
2cc. standard.	2cc. standard.		
100	66	71	
	68	70	67
	73	75	64
	68	68	65
	70	73	67
	<u>70</u>	74	66
	<u>345</u>	<u>441</u>	<u>329</u>
	av. <u>69</u>	av. <u>73.5</u>	av. <u>65.8</u>

Spilman.		Jackson.	After Jackson.
(m) 3-29-12.			
Standard tube.	Unknown tube.		
80% alcohol.	80% alcohol.		
2cc. standard.	2cc. standard.		
100	94	95	
	89	100	
	96	104	
	92	98	91
	89	98	92
	<u>460</u>	101	90
	av. 92	102	95
		<u>105</u>	<u>91</u>
		803	<u>459</u>
		av. 100.4	av. 91.8

From this Table 8 it can be concluded without a doubt that decreasing the strength of alcohol decreases the strength of color of the solution and that for accurate results both tubes must be brought to the mark with the same strength of alcohol.

The second point to be investigated was the terpeneless lemon extracts themselves. The object was to determine the method of making a legal terpeneless extract of lemon in the most economical manner. Several series of extracts were made, containing different percentages of lemon oil and different strengths of alcohol.

In making an extract the lemon oil, 5, 10 or 15 cc., was pipetted into a 100 cc. graduated flask and the amount of strong alcohol necessary to make the strength desired added by means of a burette. This strong alcohol dissolved the oil but when water was added to complete the 100 cc., the more insoluble terpenes were thrown out of solution. The flask was fitted with a two hole rubber stopper through which was a short glass tube ending with the cork and a longer glass tube extending to the bottom of the flask. A small rubber tube with a pinch cock was attached to the shorter glass tube and the flask inverted. The flask was allowed to remain so for a day and the insoluble oil rose to the top. The clear extract was drawn off by means of the pinch cock and filtered. Twenty five grams of the clear solution were weighed into a 50 cc. graduated flask and the volume completed to the mark with strong alcohol.

The citral used in making the standard solution and the lemon oil from which the extracts were made were both purchased from Fritzsche Brothers of New York.

Three series of extracts were made. The first contained 5% of lemon oil and the extracts were made with 90 - 80 - 70 - 60 - 50 - 40 - 30 - 20% alcohol. The second contained 10% lemon oil and had 80 - 60 - 40 - 20% alcohol. The third was 15% lemon oil and also had 80 - 60 40 and 20% alcohol. The analyses of these extracts are now given.

5% LEMON OIL. 90% ALCOHOL.

(a) 3-2-12.

(b) 3-2-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
2cc. standard. 2cc. extract. 2cc. standard. 2cc. extract.

100

103

100

96

96

94

101

93

99

89

94

92

493

464

av. 98.6

av. 92.8

(c) 3-4-12.

(d) 3-8-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
2cc. standard. 1.7 cc. ext. 2cc. standard. 1.6 cc. ext.

100

99

100

102

98

96

100

98

96

96

100

99

493

491

av. 98.6

av. 98.2

(e) 3-8-12.

Standard tube. Unknown tube.
2cc.standard. 1.5 cc. ext.

100	99
	98
	100
	97
	<u>102</u>
	<u>496</u>
av.	<u>99.2</u>

Per cent of citral equals .26%.

5% LEMON OIL. 80% ALCOHOL.

(a) 3-8-12.

Standard tube. Unknown tube.
2cc.standard. 2cc.extract.

100	95
	90
	94
	90
	95
	90
	91
	94
	92
	<u>831</u>
av.	<u>92.3</u>

(b) 4-12-12.

Standard tube. Unknown tube.
2cc.standard. 2cc.extract.

100	80
	81
	79
	81
	<u>83</u>
	<u>404</u>
av.	<u>80.8</u>

(c) 4-12-12.

Standard tube. Unknown tube.
2cc.standard. 1.5 cc. ext.

100	100
	101
	102
	97
	<u>100</u>
	<u>500</u>
av.	<u>100</u>

(d) 4-12-12.

Standard tube. Unknown tube.
2cc.standard. 1.5 cc. ext.

100	105
	98
	100
	104
	104
	104
	106
	<u>721</u>
av.	<u>103</u>

(e) 4-19-12.

Standard tube. Unknown tube.
2cc.standard. 1.5 cc. ext.

100	90
	90
	89
	88
	92
	<u>489</u>
	av. <u>89.8</u>

(f) 4-19-12.

Standard tube. Unknown tube.
2cc.standard. 1.2 cc. ext.

100	109
	106
	110
	110
	114
	110
	<u>111</u>
	<u>770</u>
	av. <u>110</u>

(g) 4-19-12.

Standard tube. Unknown tube.
2cc. standard. 1.3 cc. ext.

100	110
	109
	112
	111
	110
	<u>552</u>
	av. <u>110.4</u>

(h) 4-19-12.

Standard tube. Unknown tube.
2cc.standard. 1.5 cc. ext.

100	96
	92
	100
	94
	96
	96
	<u>100</u>
	<u>674</u>
	av. <u>96.3</u>

(i) 4-19-12.

Standard tube. Unknown tube.
2cc.standard. 1.4 cc. ext.

100	100
	97
	101
	98
	101
	98
	<u>102</u>
	<u>697</u>
	av. <u>99.5</u>

Percentage of citral equals .26%.

5% LEMON OIL. 70% ALCOHOL.

(a) 3-8-12.

(b) 3-8-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. 2.1 cc. ext. 2cc. standard. 1.8 cc. ext.

100	90	100	96
	96		93
	98		99
	92		95
	94		96
	<u>470</u>		<u>479</u>
	av. 94.		av. 95.8

(c) 4-12-12.

(d) 4-12-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. 2cc. extract. 2cc. standard. 1.7 cc. ext.

100	90	100	100
	94		98
	92		100
	89		99
	90		100
	91		<u>497</u>
	92		av. 99.4
	<u>638</u>		
	av. 91.1		

Percentage of citral equals .235%.

5% LEMON OIL. 60% ALCOHOL.

(a) 3-7-12.

(b) 4-15-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. 2.2 cc. ext. 2cc. standard. 2cc. extract.

100	100	100	89
	91		86
	97		86
	93		86
	94		89
	93		<u>436</u>
	94		av. 87.2
	<u>662</u>		
	av. 94.		

(c) 4-15-12.		(d) 4-15-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
2cc. standard.	1.5 cc. ext.	2cc. standard.	1.7 cc. ext.
100	104	100	103
	123		103
	118		106
	119		97
	116		105
	112		105
	118		105
	<u>810</u>		<u>724</u>
	av. 115.7		av. 103.2

(e) 4-15-12.	
Standard tube.	Unknown tube.
2cc. standard.	1.8 cc. ext.
100	104
	96
	97
	102
	101
	102
	<u>101</u>
	<u>703</u>
	av. 100.4

Percentage of citral equals .22%.

5% LEMON OIL. 50% ALCOHOL.

(a) 4-15-12.		(b) 4-15-12.	
Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
2cc. standard.	2cc. extract.	2cc. standard.	2.2 cc. ext.
100	120	100	104
	114		110
	120		106
	121		107
	118		106
	120		<u>533</u>
	118		av. 106.6
	<u>831</u>		
	av. 118.7		

(c) 4-15-12.

(d) 4-15-12

Standard tube. Unknown tube. Standard tube. Unknown tube.
 2cc. standard. 2.3 cc. ext. 2cc. standard. 2.4cc. ext.

100	100	100	102
	104		103
	102		100
	99		100
	100		101
	102		99
	100		100
	<u>707</u>		<u>705</u>
	av. 101.		av. 100.7

Percentage of citral equals .16%.

5% LEMON OIL. 40% ALCOHOL.

(a) 4-15-12.

(b) 4-18-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
 2cc. standard. 3cc. extract. 2cc. standard. 4cc. extract.

100	126	100	97
	122		94
	122		93
	126		92
	<u>125</u>		91
	<u>621</u>		92
	av. 124.2		90
			<u>649</u>
			av. 92.7

(c) 4-18-12.

Standard tube. Unknown tube.
 2cc. standard. 3.6cc. ext.

100	100
	101
	99
	101
	98
	<u>499</u>
	av. 99.8

Percentage of citral equals .11%.

5% LEMON OIL. 30% ALCOHOL.

(a) 4-18-12.

(b) 4-18-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. 7cc extract. 2cc. standard. 7.5 cc. ext.

100	118	100	118
	112		118
	108		117
	110		118
	107		<u>116</u>
	108		<u>587</u>
	<u>105</u>		av. <u>117.4</u>
	<u>768</u>		
	av. <u>109.7</u>		

(c) 4-19-12.

(d) 4-19-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. 8cc. extract. 2cc. standard. 8.4cc. ext.

100	108	100	106
	106		106
	110		106
	108		108
	<u>106</u>		<u>106</u>
	<u>538</u>		<u>532</u>
	av. <u>107.6</u>		av. <u>106.4</u>

(e) 4-19-12.

Standard tube. Unknown tube.

1cc. standard. 4.7 cc. ext.

100	98
	96
	96
	100
	<u>99</u>
	<u>489</u>
	av. <u>97.8</u>

Percentage of citral equals .04%.

5% LEMON OIL. 20% ALCOHOL.

(a) 4-19-12.

(b) 4-19-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

1cc. standard. 8cc. extract. 1cc. standard. 10cc. ext.

100	112	100	104
	118		102
	120		100
	110		100
	<u>113</u>		101
	<u>573</u>		102
	av. 114.6		98
			<u>707</u>
			av. 101.

Percentage of citral equals .02%.

10% LEMON OIL. 80% ALCOHOL.

(a) 5-3-12.

(b) 5-6-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc. standard. .75cc. ext. 2cc. standard. .75cc. ext.

100	104	100	107
	98		107
	103		108
	97		103
	100		<u>108</u>
	97		<u>533</u>
	<u>100</u>		av. 106.6
	<u>699</u>		
	av. 99.8		

(c) 5-6-12.

Standard tube. Unknown tube.

2cc. standard. .8 cc. ext.

100	104
	107
	104
	105
	<u>107</u>
	<u>527</u>
	av. 105.4

Percentage of citral equals .53%.

10% LEMON OIL. 60% ALCOHOL.

(a) 5-3-12.

(b) 5-3-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
 2cc. standard. 1.5 cc. ext. 2cc. standard. 1cc. extract.

100	74
	74
	74
	75
	70
	<u>367</u>
	av. 73.4

100	99
	106
	103
	103
	100
	103
	100
	<u>714</u>
	av. 102.

(c) 5-3-12.

Standard tube. Unknown tube.
 2cc. standard. 1.1 cc. ext.

100	92
	94
	96
	92
	96
	<u>470</u>
	av. 94

Percentage of citral equals .40%.

10% LEMON OIL. 40% ALCOHOL.

(a) 5-3-12.

(b) 5-3-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
 2cc. standard. 2.5 cc. ext. 2cc. standard. 3cc. extract.

100	112
	110
	112
	110
	<u>112</u>
	<u>556</u>
	av. 111.2

100	94
	94
	96
	92
	94
	<u>470</u>
	av. 94.

(c) 5-3-12.

(d) 5-3-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
 2cc.standard. 2.7 cc. ext. 2cc.standard. 2.8 cc. ext.

100	106	100	98
	106		97
	104		102
	103		104
	102		103
	100		96
	<u>106</u>		<u>102</u>
	<u>727</u>		<u>702</u>
	av. 103.8		av. 100.2

Percentage of citral equals .14%.

10% LEMON OIL. 20% ALCOHOL.

(a) 5-3-12.

Standard tube. Unknown tube.

1cc.standard. 9cc.extract.

100	110
	108
	100
	102
	96
	108
	<u>102</u>
	<u>726</u>
	av. 103.7

Percentage of citral equals .02%.

15% LEMON OIL. 80% ALCOHOL.

(a) 5-6-12.

(b) 5-6-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc.standard. .5 cc. ext. 2cc.standard. .6 cc. ext.

100	107	100	93
	107		93
	98		93
	98		95
	100		<u>90</u>
	98		<u>464</u>
	<u>104</u>		av. 92.8
	<u>712</u>		
	av. 101.7		

Percentage of citral equals .80%.

15% LEMON OIL. 60% ALCOHOL.

(a) 5-6-12.

(b) 5-6-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.

2cc.standard. .75 cc. ext. 2cc.standard. .6 cc. ext.

100	88	100	108
	89		107
	88		113
	88		109
	89		108
	<u>442</u>		<u>545</u>
	av. 88.4		av. 109.

(c) 5-6-12.

Standard tube. Unknown tube.

2cc.standard. .65 cc. ext.

100	102
	100
	101
	101
	101
	<u>505</u>
	av. 101.

Percentage of citral equals .61%.

15% LEMON OIL. 40% ALCOHOL.

(a) 5-6-12.

Standard tube. Unknown tube.

2cc.standard. 2cc.extract.

100	101
	100
	100
	100
	102
	<u>503</u>
	av. 100.6

Percentage of citral equals .2%.

15% LEMON OIL. 20% ALCOHOL.

(a) 5-6-12.

(b) 5-6-12.

Standard tube. Unknown tube. Standard tube. Unknown tube.
 1cc. standard. 7cc. extract. 1cc. standard. 6.5 cc. ext.

100	89	100	100
	90		97
	96		95
	90		96
	92		92
	<u>457</u>		96
	av. 91.4		97
			<u>673</u>
			av. 96.1

Percentage of citral equals .03%.

The percentages of citral were calculated from the number of cubic centimeters of extract solution used by the following formula.

$$y : 2 :: .2 : x$$

y is number of cc. of extract solution.

x is per cent. of citral in original extract.

This formula is based on using 2cc. standard citral solution.

The results of the analyses of the extracts just given are collected in the form of a table and of a plot. In this plot the per cent. of citral is plotted against the per cent. of alcohol for the three different per cents of lemon oil.

More exact results of some of these extracts.

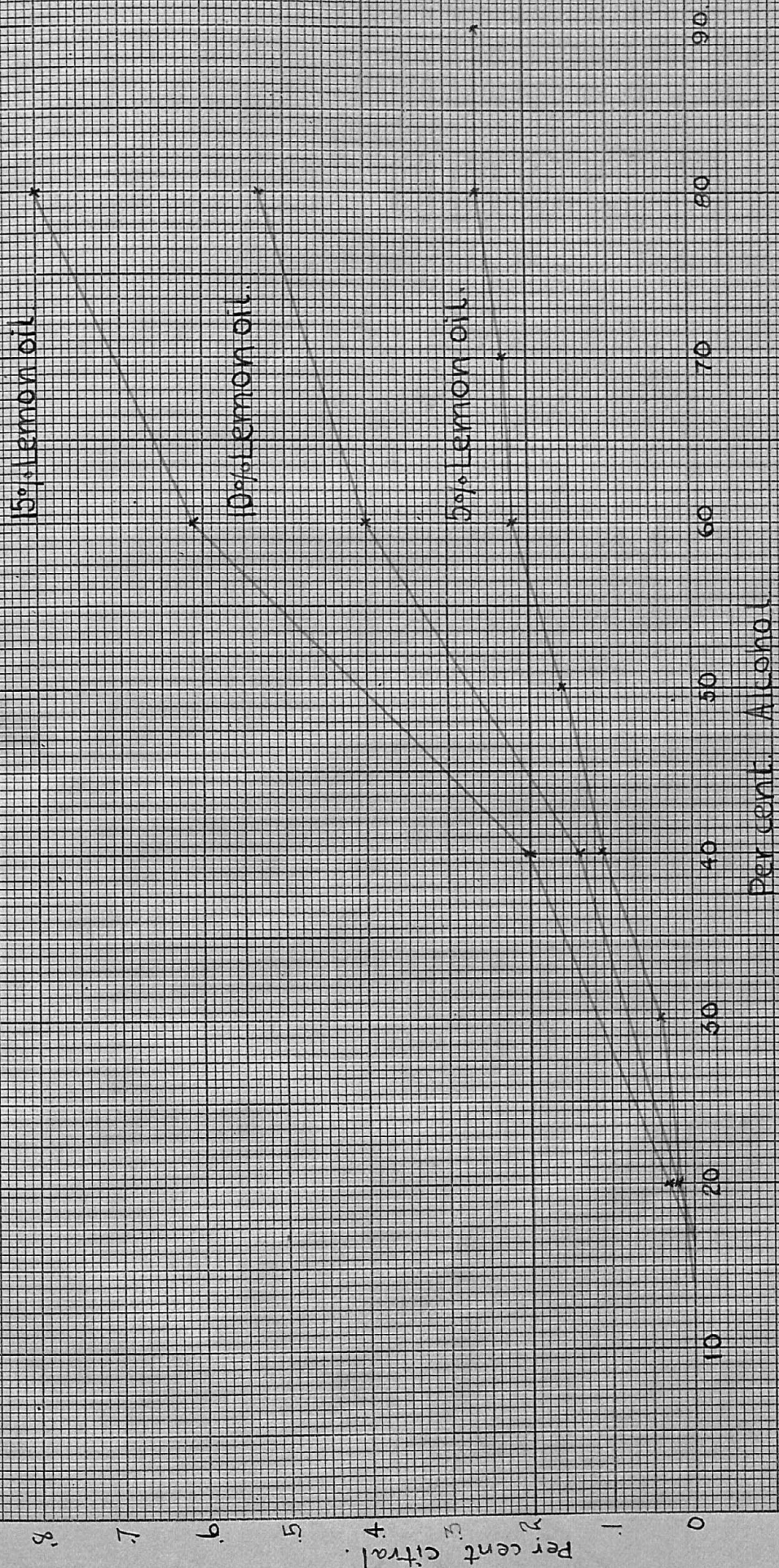
5% Lemon oil	90% Alcohol.	Citral	.266%
5% " "	80% " "	" "	.272%
5% " "	70% " "	" "	.235%
5% " "	50% " "	" "	.166%
10% " "	40% " "	" "	.146%
15% " "	60% " "	" "	.615%

Table showing variation of citral per cent. in extracts containing different per cents of lemon oil and alcohol. A summary of the previous data.

5% LEMON OIL.		10% LEMON OIL.		15% LEMON OIL.	
% alcohol.	% citral.	% citral found.	% citral cal.	% citral found.	% citral cal.
90	.26				
80	.26	.53	.52	.80	.78
70	.23				
60	.22	.40	.44	.61	.66
50	.16				
40	.11	.14	.22	.20	.33
30	.04				
20	.02	.02	.04	.03	.06

A study of this table and plot shows several things. There seems to be a per cent of alcohol which is about 17% in which no citral is dissolved. In other words the solubility of citral in 17% alcohol is zero. The solubility of citral in 20% alcohol is shown to be .02%. When the strength of alcohol is along between 80 and 90% the citral content varies directly as the percentage of lemon oil which shows that the lemon oil was entirely dissolved.

In the plot the line representing the .2% citral is the border line between a legal or an illegal terpeneless lemon extract. No combination below this line can be considered. From Merk's Report of May 1912 the follow-



ing data was obtained. Lemon oil costs \$2.00 for one pound. Ethyl alcohol, 95%, costs \$3.10 for one gallon. From this data the cost of one liter of extract was calculated. The specific gravity of the lemon oil was taken as $\frac{1}{.859}$.

Taking 454 as the number of grams in one pound and assuming that 1 cc. weighs .859 gm. the cost of 1 cc. of lemon oil is

$$\frac{.859 \times 200}{454} = .378 \text{ cents / cc.}$$

Since there are 3780 cc. in one gallon, 1 cc. of 95% alcohol costs .082 cents. 1.052 cc. of 95% alcohol equals 1 cc. of absolute alcohol. The following are the calculated costs of lemon oil and alcohol for one liter of extract that would be above standard.

5% lemon oil.	50 x .378	18.90
60% alcohol.	600 x 1.052 x .082	<u>51.76</u>
		70.66 cents.
10% lemon oil.	100 x .378	37.80
50% alcohol.	500 x 1.052 x .082	<u>43.13</u>
		80.93 cents.
15% lemon oil.	150 x .378	56.70
40% alcohol.	400 x 1.052 x .082	<u>34.50</u>
		91.20 cents.
5% lemon oil.	50 x .378	18.90
55% alcohol.	550 x 1.052 x .082	<u>47.44</u>
		66.34 cents.

1. Parry, Ernest J. The Chemistry of Essential Oils,
1908, page 528.

An increase of 1% of lemon oil per liter costs 3.78 cents while an increase of 5% of alcohol costs 4.4 cents.

The above figures indicate that a 5% lemon oil 55% alcohol extract would be the cheapest. Such an extract was made and tested for strength with the following results.

(a) 5-13-12.

(b) 5-13-12.

Standard tube.	Unknown tube.	Standard tube.	Unknown tube.
2cc. standard.	2cc. extract.	2cc. standard.	2.2 cc. ext.

100

110

100

100

106

100

104

104

106

100

105

98

531

502

av. 106.2

av. 100.4

This gives a citral per cent. of .182. This does not miss the standard far and probably would not be contested.

An extract containing 6% lemon oil and 55% alcohol was analyzed as follows.

(a) 5-15-12.

Standard tube. Unknown tube.

2cc. standard. 2cc. extract.

100

90

91

86

87

88

88

530

av. 88.3

This shows that this extract is well above standard. The cost of this extract is 70.08 cents per liter.

An extract was made which contained 6% lemon oil and 50% alcohol. Its analysis is as follows.

Standard tube. Unknown tube.

2cc. standard. 2cc. extract.

100	101
	101
	102
	100
	<u>102</u>
	506
	av. 101.2

This is so near standard that no objections to it could be raised. The lemon oil and alcohol for this extract costs 65.68 cents. for one liter. From this data this is the cheapest extract that is standard that can be made. Additional data might show a slight lowering.

Experiments were next conducted along the lines of distillation. When lemon oil is freed wholly or in part from its terpenes it dissolves easily in dilute alcohol. If some easy method of separating the citral from the terpenes could be obtained it would effect a great saving in the alcohol.

Distillation in vacuum was attempted. Two 50 cc. Jena distilling flasks were connected together with a rubber cork and connected through a manometer to a filter pump. A pressure of 27 mm. of mercury was obtained. The lemon oil boiled at from 79 to 82 degrees C. The distilling flask was heated in an oil bath and the receiving

flask was cooled by running water. The distillation was continued until the temperature began to recede from 82 degrees C. Twenty five cubic centimeters of lemon oil were taken to start with and there were 1.6 cc. in the residue and 23 cc. in the distillate. One fifth of the residue and distillate were each taken and made into extracts of 100 cc. with alcohol strong enough to dissolve them. These extracts were analyzed in the usual way. The extract from the residue contained .12% citral while the extract from the distillate contained .09%. This shows that a great concentration of citral was effected but hardly great enough to be profitable. Distillation under atmospheric pressure resulted in the residue decomposing into a dark red, gummy liquid. Fractionation under diminished pressure was next tried.

A straight adapter was filled with metallic, scrap tin and fitted by rubber stoppers into a 50 cc. balloon flask. At a pressure of 67 mm. of mercury the distillate began coming over at 32 degrees C. The temperature gradually rose to 84 degrees C. and then receded. Twenty five cubic centimeters of lemon oil were taken to begin with and the residue contained 2.6 cc. and the distillate 18 cc. A fifth of each was taken and made ~~into~~ into an extract. The analysis seemed to show that the extract from the residue contained .30% of citral while 10 cc. of the extract solution from the distillate failed to deepen the color of the meta phenylene diamine solution.

Lack of time prevented this thesis from being continued. These last results seem to show that this problem may be solved by some simple fractionation method.

In conclusion it can be said that ~~this~~ thesis has shown that in the Hiltner method for the determination of citral both tubes must be made up with the same strength of alcohol since the color of the meta phenylene diamine solution decreases as the strength of alcohol decreases. It has also shown that a standard terpeneless lemon extract can be made containing 6% lemon oil and 50% alcohol at a cost for these materials of 65.68 cents for one liter of extract.

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