A Study of Terpeneless Lemon Extracts

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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.

1208 Mississippi St.

Lawrence, Kansas.

May 27, 1912.

To the Falculty 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 Jackson[1] 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's[2] 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 diamin

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 diamin 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 diamin 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 diamin hydrochlorid solution was not treated with fuller's earth or animal charcoal because it has been found[1] that this treatment sometimes augments the color rather than reduces it. The salt was weighed within a hundreth 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 ee.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 diamin 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.

Standard tube. 86% alcohol 2cc.standard.	Unknown tube 70% alcohol. 2cc.standard.
100	109
	102
	110
	100
	106
	527
	av 105.4

(b) 3-8-12.

Standard tube. 86% alcohol. 2cc.standard.	Unknown tube 40% alcohol 2cc.standard
100	112
	108
	115
	110
	114
	559
	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
	587		496
	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 diamin 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.

Standard tube. 94.5I% alcohol No citral	Unknown tube. 70% alcohol. no citral
100	94
	92
	91
	93
	90
	460
	av. 92

(b) 3-9-12.

Standard tube. 94.5I% alcohol no citral	Unknown tube. 50% alcohol. no citral.
100	90.
	94
	93
	96
	98
	471
	av. 94.2

(c) 3-9-12.

Standard tube. 94.5I% alcohol no citral.	Unknown tube. 40% alcohol. no citral.
100	109
	101
	113
	108
	109
	540
	av. 108

(d) 3-9-12.

Standard tube. 94.51% alcohol no citral.	Unknown tube. 20% alcohol. no citral.
100	78
	72
	71
	72
	80
	373
	av. 74.6

(e) 3-9-12.

Standard tube. 94.5I% alcohol no citral.	Unknown tube. 94.51% alcohol. no citral.
100	103
	102
	100
	102
	102
	509
	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.

Standard tube. 94.51% alcohol 2 cc.standard.	Unknown tube. 50% alcohol. 2cc.standard.
100	118
	114
	116
	113
	113
	574
	av.114.8

(b) 3-9-12.

Standard tube. 94.51% alcohol 2cc.standard.	Unknown tube. 40% alcohol. 2cc.standard.
100	126
	124
	127
	120
	124
	621
	av.124.2

(c) 3-9-12.

Standard tube. 94.51% alcohol 2cc.standard.	Unknown tube. 20% alcohol. 2cc.standard.
100	122
	Other readings 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 there abouts 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.

Standard tube. 90% alcohol. no citral.	Unknown tube. 90% alcohol. no citral.
100	101
	99
	104
	98
	99
	501
	av. 100.2

(b) 3-15-12.

Same as (a) but tubes changed in colorimeter.

100	100
	97
	106
	100
	93
	496
	av. 99.2

(c) 3-15-12.

Standard tube. 80% alcohol. no citral.	Unknown tube. 80% alcohol. no citral.
100	96
	98
	93
	94
	91
	472
	av. 94.4

(d) 3-15-12.

Standard tube. 50% alcohol. no citral.	Unknown tube. 50% alcohol. no citral.
100	100
	104
	96
	100
	96
	101
	597
	av. 99.5

(e) 3-15-12.

Standard tube. 80% alcohol. no citral.	Unknown tube. 80% alcohol. no citral.
100	96
	97
	96
	100
	93
	100
	96
	678
	av. 96.8

(f) 3-15-12.

Standard tube. 40% alcohol. no citral.	Unknown tube. 40% alcohol. no citral.
100	96
	106
	100
	102
	103
	507
	av. 101.4

(g) 3-15-12.

Standard tube. 90% alcohol. no citral.	Unknown tube. 90% alcohol. no citral.
100	99
	99
	98
	94
	100
	96
	104
	690
	av. 98.5

(h) 3-15-12.

Standard tube. 80% alcohol. no citral.	Unknown tube. 80% alcohol. no citral.
100	99
	102
	97
	102
	99
	~~499~~
	av. 99.8

(i) 3-15-12.

Standard tube. 50% alcohol. no citral.	Unknown tube. 50% alcohol. no citral.
100	96
	97
	104
	106
	97
	500
	av. 100

(j) 3-15-12.

Standard tube. 40% alcohol. no citral.	Unknown tube. 40% alcohol. no citral.
100	102
	103
	95
	97
	94
	491
	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.

Standard tube. 90% alcohol. no citral.	Unknown tube. 80% alcohol. no citral.
100	108
	101
	98
	101
	100
	508
	av.101.6

(b) 3-22-12.

Standard tube. 90% alcohol. no citral.	Unknown tube. 50% alcohol. no citral.
100	104
	104
	102
	102
	106
	518
	av.103.6

(c) 3-22-12.

Standard tube. 90% alcohol. no citral.	Unknown tube. 40% alcohol. no citral.
100	100
	108
	111
	100
	106
	525
	av.105

(d) 3-23-12.

Standard tube. 90% alcohol. no citral.	Unknown tube. 80% alcohol. no citral.
100	104
	98
	104
	106
	103
	515
	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 diamin 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 diamin solution standard citral solution was used to develope 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.

Standard tube. 80% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	96
	97
	96
	98
	95
	482
	av. 96.4

(b) 3-23-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.
100	102
	98
	116
	100
	116
	532
	av. 106.4

(c) 3-23-12.

Standard tube. 40% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.
100	96
	90
	90
	96
	98
	464
	av. 92.8

(d) 3-23-12.

Standard tube. 30% alochol. 2cc. standard.	Unknown tube. 30% alcohol. 2cc. standard
100	109
	100
	99
	103
	96
	507
	av. 101.4

(e) 3-23-12.

Standard tube. 80% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	96
	99
	102
	99
	94
	490
	av. 98

(f) 3-23-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.
100	97
	97
	98
	101
	94
	487
	av. 97.4

(g) 3-23-12.

Standard tube. 40% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.
100	97
	100
	100
	98
	98
	493
	av. 98.6

(h) 3-23-12.

Standard tube. 30% alcohol. 2cc. standard.	Unknown tube. 30% alcohol. 2cc. standard.
100	94
	100
	106
	104
	106
	510
	av. 102

(i) 3-25-12.

Standard tube. 80% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	103
	96
	94
	95
	97
	485
	av. 97

(j) 3-25-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.
100	103
	92
	98
	98
	103
	494
	av. 98.8

(k) 3-25-12.

Standard tube. 40% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.
100	106
	103
	98
	93
	103
	503
	av. 100.6

(l) 3-25-12.

Standard tube. 80% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	102
	97
	100
	94
	96
	489
	av. 99.8

(m) 3-25-12.

Standard tube.	Unknown tube.
50% alcohol.	50% alcohol.
2cc.standard.	2cc.standard.
100	93
	102
	93
	98
	96
	482
	av. 96.4

(n) 3-25-12.

Standard tube.	Unknown tube.
40% alcohol.	40% alcohol.
2cc.standard.	2cc.standard.
100	91
	94
	95
	97
	101
	478
	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
	487
	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
	485
	av. 97

(q) 3-25-12.

Standard tube.	Unknown tube.
50% alcohol.	50% alcohol.
2cc.standard.	2cc.standard.
100	97
	97
	94
	95
	90
	473
	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
	475
	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.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	66
	70
	67
	65
	64
	332
	av. 66.4

(b) 3-28-12.

Standard tube. 50% alcohol 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.
100	102
	98
	94
	95
	93
	482
	av. 96.4

(c) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.
100	104
	98
	106
	100
	102
	510
	av. 102

(d) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 30% alcohol. 2cc. standard.
100	116
	110
	120
	110
	118
	574
	av. 114.8

(e) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 80% alcohol. 2cc. standard.
100	74
	65
	72
	74
	66
	351
	av. 70.2

(f) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.
100	97
	96
	97
	102
	98
	490
	av. 98

(g) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.
100	108
	106
	106
	104
	105
	529
	av. 105.8

(h) 3-28-12.

Standard tube. 50% alcohol. 2cc. standard.	Unknown tube. 30% alcohol. 2cc. standard.
100	113
	110
	114
	110
	114
	561
	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[1] 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.	
100	94	95
	96	94
	90	97
	92	94
	90	94
	462	92
	av. 92.4	660
		av. 94.3
(b) 3-29-12.		
Standard tube.	Unknown tube.	
80% alcohol.	80% alcohol.	
2cc.standard.	2cc.standard.	
100	96	97
	94	98
	94	103
	93	101
	92	97
	471	103
	av. 94.2	100
		102
		801
		av.100.1
(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	101
	467	498
	av. 93.4	av. 99.6

Spilman. Jackson. After Jackson.

(d) 3-29-12.

Standard tube. 40% alcohol. 2cc. standard.	Unknown tube. 40% alcohol. 2cc. standard.		
100	98	100	98
	100	99	99
	96	98	95
	100	102	90
	92	100	94
	486	499	476
	av. 97.2	av. 99.8	av. 95.2

(e) 3-29-12.

Standard tube. 80% alcohol. 2cc. standard.	Unknown tube. 50% alcohol. 2cc. standard.		
100	78	74	69
	78	72	68
	79	74	72
	71	72	69
	74	74	75
	380	366	353
	av. 76	av. 73.2	av. 70.6

(f) 3-29-12.

Standard tube. 30% alcohol. 2cc. standard.	Unknown tube. 30% alcohol. 2cc. standard.		
100	103	103	97
	98	101	100
	95	100	97
	98	101	98
	98	102	94
	483	507	486
	av. 96.6	av. 101.4	av. 97.2

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
	546	825	538
	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
	453	500	466
	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
	498	500	488
	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.	104	
		100	
100	99	105	92
	95	102	100
	92	101	94
	97	103	97
	94	104	98
	477	719	481
	av. 95.4	av.102.7	av. 96.2
(k) 3-29-12.			
Standard tube.	Unknown tube.		
40% alcohol,	50% alcohol,	109	
		109	
2cc.standard.	2cc.standard.	114	
		109	
100	100	104	100
	101	106	102
	107	103	98
	106	107	105
	106	103	98
	520	966	503
	av.104	av.107	av.100.6
(l) 3-29-12,			
Standard tube.	Unknown tube.		
80% alcohol.	50% alcohol.		
2cc.standard.	2cc.standard.		
		71	
100	66	70	67
	68	75	64
	73	68	65
	68	73	67
	70	74	66
	345	441	329
	av. 69	av. 73.5	av. 65.8

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

Standard tube. 2cc. standard.	Unknown tube. 2cc. extract.
100	103
	96
	101
	99
	94
	493
	av. 98.6

(b) 3-2-12.

Standard tube. 2cc. standard.	Unknown tube. 2cc. extract.
100	96
	94
	93
	89
	92
	464
	av. 92.8

(c) 3-4-12.

Standard tube. 2cc. standard.	Unknown tube. 1.7 cc. ext.
100	99
	98
	100
	96
	100
	493
	av. 98.6

(d) 3-8-12.

Standard tube. 2cc. standard.	Unknown tube. 1.6 cc. ext.
100	102
	96
	98
	96
	99
	491
	av. 98.2

(e) 3-8-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	99
	98
	100
	97
	102
	496
	av. 99.2

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
	831
	av. 92.3

(b) 4-12-12.

Standard tube.	Unknown tube.
2cc.standard.	2cc.extract.
100	80
	81
	79
	81
	83
	404
	av. 80.8

(c) 4-12-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	100
	101
	102
	97
	100
	500
	av.100

(d) 4-12-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	105
	98
	100
	104
	104
	104
	106
	721
	av.103

(e) 4-19-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	90
	90
	89
	88
	92
	449
	av. 89.8

(f) 4-19-12.

Standard tube.	Unknown tube.
2cc.standard.	1.2 cc. ext.
100	109
	106
	110
	110
	114
	110
	111
	770
	av.110

(g) 4-19-12.

Standard tube.	Unknown tube.
2cc. standard.	1.3 cc. ext.
100	110
	109
	112
	111
	110
	552
	av.110.4

(h) 4-19-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	96
	92
	100
	94
	96
	96
	100
	674
	av. 96.3

(i) 4-19-12.

Standard tube.	Unknown tube.
2cc.standard.	1.4 cc. ext.
100	100
	97
	101
	98
	101
	98
	102
	697
	av. 99.5

Percentage of citral equals .26%.

5% LEMON OIL. 70% ALCOHOL.

(a) 3-8-12.

Standard tube.	Unknown tube.
2cc. standard.	2.1 cc. ext.
100	90
	96
	98
	92
	94
	470
	av. 94.

(b) 3-8-12.

Standard tube.	Unknown tube.
2cc. standard.	1.8 cc. ext.
100	96
	93
	99
	95
	96
	479
	av. 95.8

(c) 4-12-12.

Standard tube.	Unknown tube.
2cc. standard.	2cc. extract.
100	90
	94
	92
	89
	90
	91
	92
	638
	av. 91.1

(d) 4-12-12.

Standard tube.	Unknown tube.
2cc. standard.	1.7 cc. ext.
100	100
	98
	100
	99
	100
	497
	av. 99.4

Percentage of citral equals .23%.

5% LEMON OIL. 60% ALCOHOL.

(a) 3-7-12.

Standard tube.	Unknown tube.
2cc. standard.	2.2 cc. ext.
100	100
	91
	97
	93
	94
	93
	94
	662
	av. 94.

(b) 4-15-12.

Standard tube.	Unknown tube.
2cc. standard.	2cc. extract.
100	89
	86
	86
	86
	89
	436
	av. 87.2

(c) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	1.5 cc. ext.
100	104
	103
	118
	119
	116
	112
	118
	810
	av.115.7

(d) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	1.7 cc. ext.
100	103
	103
	106
	97
	105
	105
	105
	724
	av.103.2

(e) 4-1512.

Standard tube.	Unknown tube.
2cc.standard.	1.8 cc. ext.
100	104
	96
	97
	102
	101
	102
	101
	703
	av.100.4

Percentage of citral equals .22%.

5% LEMON OIL. 50% ALCOHOL.

(a) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	2cc.extract.
100	120
	114
	120
	121
	118
	120
	118
	831
	av.118.7

(b) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	2.2 cc. ext.
100	104
	110
	106
	107
	106
	533
	av.106.6

(c) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	2.3 cc. ext.
100	100
	104
	102
	99
	100
	102
	100
	707
	av.101.

(d) 4-15-12

Standard tube.	Unknown tube.
2cc.standard.	2.4cc. ext.
100	102
	103
	100
	100
	101
	99
	100
	705
	av.100.7

Percentage of citral equals .16%.

5% LEMON OIL. 40% ALCOHOL.

(a) 4-15-12.

Standard tube.	Unknown tube.
2cc.standard.	3cc.extract.
100	126
	122
	122
	126
	125
	621
	av.124.2

(b) 4-18-12.

Standard tube.	Unknown tube.
2cc.standard.	4cc.extract.
100	97
	94
	93
	92
	91
	92
	90
	649
	av. 92.7

(c) 4-18-12.

Standard tube.	Unknown tube.
2cc.standard.t	3.6cc. ext.
100	100
	101
	99
	101
	98
	499
	av. 99.8

Percentage of citral equals .11%.

5% LEMON OIL. 30% ALCOHOL.

(a) 4-18-12.

Standard tube.	Unknown tube.
2cc. standard.	7cc extract.
100	118
	112
	108
	110
	107
	108
	105
	768
	av. 109.7

(b) 4-18-12.

Standard tube.	Unknown tube.
2cc. standard.	7.5 cc. ext.
100	118
	118
	117
	118
	116
	587
	av. 117.4

(c) 4-19-12.

Standard tube.	Unknown tube.
2cc. standard.	8cc. extract.
100	108
	106
	110
	108
	106
	538
	av. 107.6

(d) 4-19-12.

Standard tube.	Unknown tube.
2cc. standard.	8.4cc. ext.
100	106
	106
	106
	108
	106
	532
	av. 106.4

(e) 4-19-12.

Standard tube.	Unknown tube.
1cc. standard.	4.7 cc. ext.
100	98
	96
	96
	100
	99
	489
	av. 97.8

Percentage of citral equals .04%.

5% LEMON OIL. 20% ALCOHOL.

(a) 4-19-12.

Standard tube.	Unknown tube.
1cc.standard.	8cc.extract.
100	112
	118
	120
	110
	113
	573
	av.114.6

(b) 4-19-12.

Standard tube.	Unknown tube.
1cc.standard.	10cc. ext.
100	104
	102
	100
	100
	101
	102
	98
	707
	av.101.

Percentage of citral equals .02%.

10% LEMON OIL. 80% ALCOHOL.

(a) 5-3-12.

Standard tube.	Unknown tube.
2cc.standard.	.75cc. ext.
100	104
	98
	103
	97
	100
	97
	100
	699
	av. 99.8

(b) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.75cc. ext.
100	107
	107
	108
	103
	108
	533
	av.106.6

(c) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.8 cc. ext.
100	104
	107
	104
	105
	107
	527
	av.105.4

Percentage of citral equals .53%.

10% LEMON OIL. 60% ALCOHOL.

(a) 5-3-12.

Standard tube.	Unknown tube.
2cc. standard.	1.5 cc. ext.
100	74
	74
	74
	75
	70
	367
	av. 73.4

(b) 5-3-12.

Standard tube.	Unknown tube.
2cc. standard.	1cc extract.
100	99
	106
	103
	103
	100
	103
	100
	714
	av. 102.

(c) 5-3-12.

Standard tube.	Unknown tube.
2cc. standard.	1.1 cc. ext.
100	92
	94
	96
	92
	96
	470
	av. 94

Percentage of citral equals .40%.

10% LEMON OIL. 40% ALCOHOL.

(a) 5-3-12.

Standard tube.	Unknown tube.
2cc. standard.	2.5 cc. ext.
100	112
	110
	112
	110
	112
	556
	av. 111.2

(b) 5-3-12.

Standard tube.	Unknown tube.
2cc. standard.	3cc. extract.
100	94
	94
	96
	92
	94
	470
	av. 94.

(c) 5-3-12.

Standard tube.	Unknown tube.
2cc.standard.	2.7 cc. ext.
100	106
	106
	104
	103
	102
	100
	106
	727
	av.103.8

(d) 5-3-12.

Standard tube.	Unknown tube.
2cc.standard.	2.8 cc. ext.
100	98
	97
	102
	104
	103
	96
	102
	702
	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
	102
	726
	av.103.7

Percentage of citral equals .02%.

15% LEMON OIL. 80% ALCOHOL.

(a) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.5 cc. ext.
100	107
	107
	98
	98
	100
	98
	104
	712
	av.101.7

(b) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.6 cc. ext.
100	93
	93
	93
	95
	90
	464
	av. 92.8

Percentage of citral equals .80%.

15% LEMON OIL. 60% ALCOHOL.

(a) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.75 cc. ext.
100	88
	89
	88
	88
	89
	442
	av. 88.4

(b) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.6 cc. ext.
100	108
	107
	113
	109
	108
	545
	av.109.

(c) 5-6-12.

Standard tube.	Unknown tube.
2cc.standard.	.65 cc. ext.
100	102
	100
	101
	101
	101
	505
	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
	503
	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
	457		96
	av. 91.4		97
			673
			av. 96.1

Percentage of citral equals .03%.

The perdentages 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.

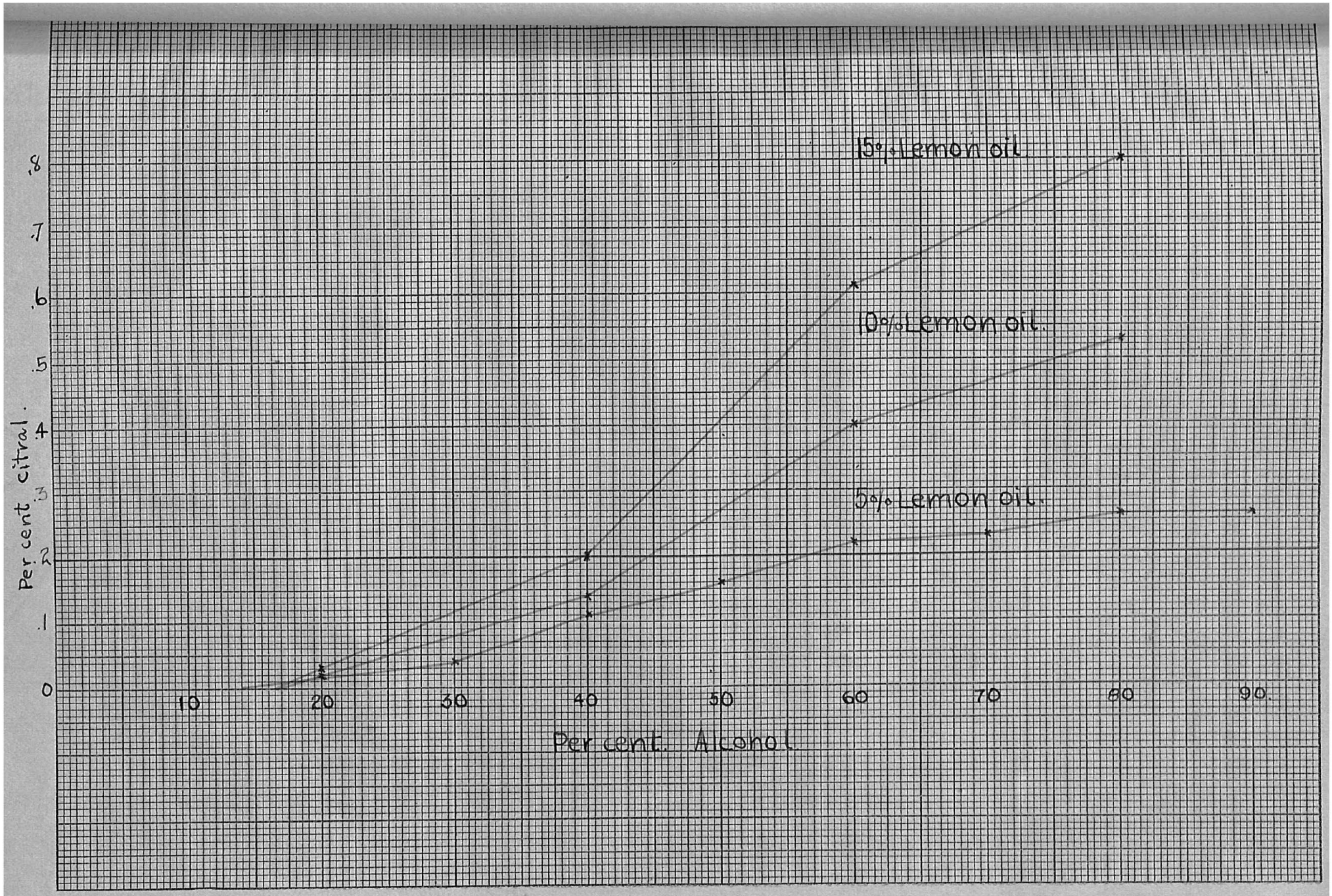
5%	Lemon oil	90%	Alcohol.	citral	.266 %
5%	" "	80%	"	"	.272 %
5%	" "	70%	"	"	.235 %
5%	" "	50%	"	"	.166 %
10%	" "	40%	"	"	.146 %
15%	" "	60%	"	"	.615 %

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-



No. 290. H. Cole Co., Columbus, Ohio

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 .859.[1]

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

Standard tube. 2cc.standard.	Unknown tube. 2cc.extract.
100	110
	106
	104
	106
	105
	531
	av. 106.2

(b) 5-13-12.

Standard tube. 2cc.standard.	Unknown tube. 2.2 cc. ext.
100	100
	100
	104
	100
	98
	502
	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 analized as follows.

(a) 5-15-12.

Standard tube. 2cc.standard.	Unknown tube. 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
	102
	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 analized 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 comming 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 diamin 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 diamin 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.