

THE EXTRACTION OF ORANGE OIL

WITH

VOLATILE SOLVENTS

Thesis

by

Willard E. Baier.

In partial fulfillment of the requirements  
for the degree of Bachelor of Science  
in Chemical Engineering.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California.

1923

THE EXTRACTION OF ORANGE OIL  
WITH  
VOLATILE SOLVENTS.

PURPOSE OF INVESTIGATION.

Citrus oils are used largely by confectioners, bakers and manufacturers of soft drinks for flavoring. In 1916, 98% of the citrus oils used in this country were imported. The relatively small amount of oils produced here are obtained from the cull fruit by two general methods, the expression or pressure method and by some form of the distillation method, either vacuum distillation of the dry peel or steam distillation under various pressures. The expression method gives a much superior oil as compared with the oil obtained by distillation. However the expression method has the disadvantage that a considerable amount of oil is left in the pulp after the squeezing process. In the plant of the Exchange Orange Products Co. at San Dimes, California, where orange oil is produced, this remaining oil is recovered in a less valuable form by a subsequent steam distillation.

The object of this investigation was to study the method of solvent extraction as a possible means of obtaining all of the oil in a good condition. A satisfactory solvent was to be found and its use studied as extensively as time permitted.

PREVIOUS WORK

A plant employing the solvent extraction method operated in Pasadena in 1902<sup>1</sup>. The peel was first crushed between rollers forming a  
-----  
R. T. Will. J. I. E. C. 8 (1916) 78-86

paste which analyzed 1.9% oil for lemons and 2.2% oil for oranges. The paste was extracted several times with solvent and the solvent was evaporated from the resultant solution. The oil was next put through some kind of refining process and was ready for the market. The solvent used and the nature of the refining process were not disclosed in the article. The oil obtained in this way contained 10.36% also resins against 5.34% in foreign hand expressed oil. This larger percentage of oleo resin was found to be advantageous because it tended to retain the volatile flavoring constituents of the oil when used in baking.

A process of expression and extraction was used on laboratory scale by H. D. Gibbs and M. V. Rosaria in their study of the Philippine orange "narangite".<sup>1</sup> The peel was first grated under water, next the liquid was pressed from the pulp through muslin, and then the pulp was extracted three times with petroleum ether. The portions of solvent were then agitated separately with the aqueous mixture and drawn off. The three portions were united and the petroleum ether was distilled at 12 to 15 mm. pressure and below 50° C.

Ethereal oils such as rose, violet, jasmine, orange blossom etc. were extracted with the following solvents, ether chloroform, carbon-tetrachloride, benzol and petroleum ether<sup>2</sup>. Petroleum ether, specific gravity 0.650, was found to be the best.

1 Phillipine Journ. Sci. Vol 7 A 6 (1912)

2 Olien, en Vetten 6 (1921) 329 Abstracted C. A. 16 (1922) 1126

## EXPERIMENTAL WORK

Solvents. A solvent for orange oil extraction must be readily miscible with the oil, volatile at low temperatures, inactive chemically toward the oil, non-poisonous and should not have a particularly unpleasant odor or taste. It would have added advantages, of course, if it were cheap and non-inflammable.

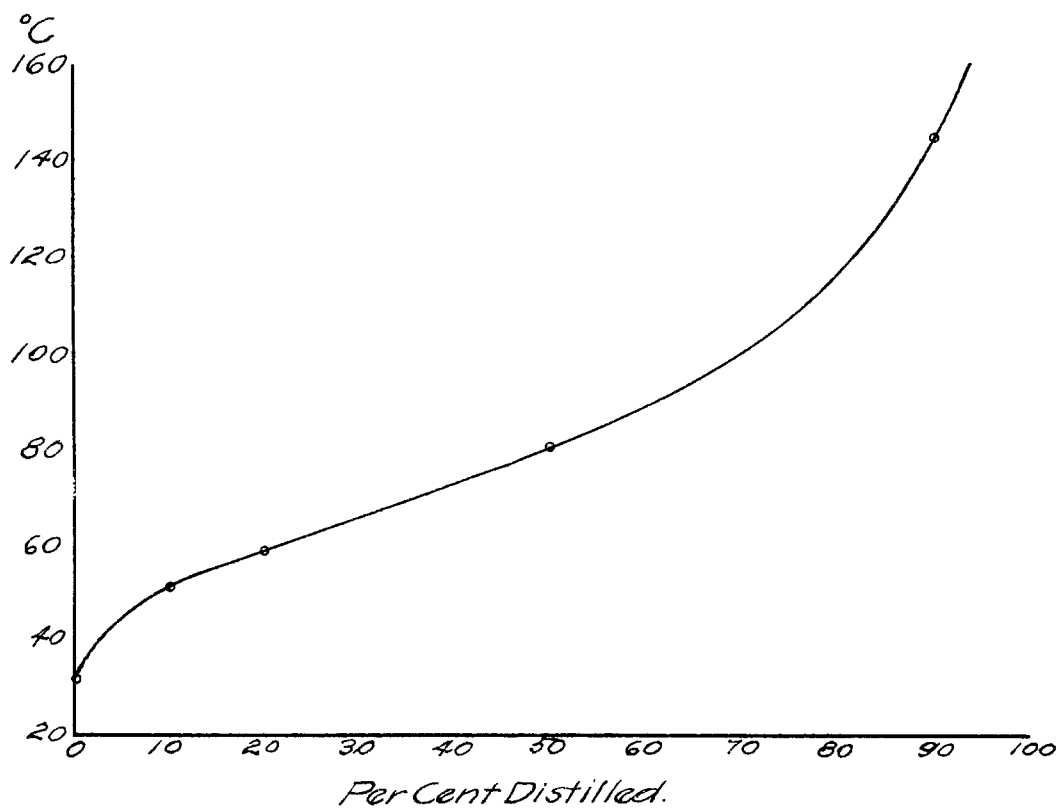
The solvents studied were commercial benzol, casing-head gasoline from the Gilmore Co., and a special gasoline fraction obtained from the Union Oil refinery at Wilmington. The benzol was found to have a very constant boiling point. A distillation test on the casing-head gasoline gave the result shown in curve I and a fractionation with a head filled Wirtz column gave the results of curve II. The specific gravity of the casing-head gasoline was 0.70. The Union Oil fraction boiled from 22-60° C and had a specific gravity of 0.632 at 15° C.

Orange Oil. The orange oil used in the work was expressed oil from the Exchange Orange Products Co. Four different samples of oil had the same refraction index,  $n_D^{20}$ , of 1.4730 and optical rotations varying from 117.0 to 117.7° in a 100 mm. tube using the yellow green mercury vapor line,  $\lambda = 5461$ , at 18°.

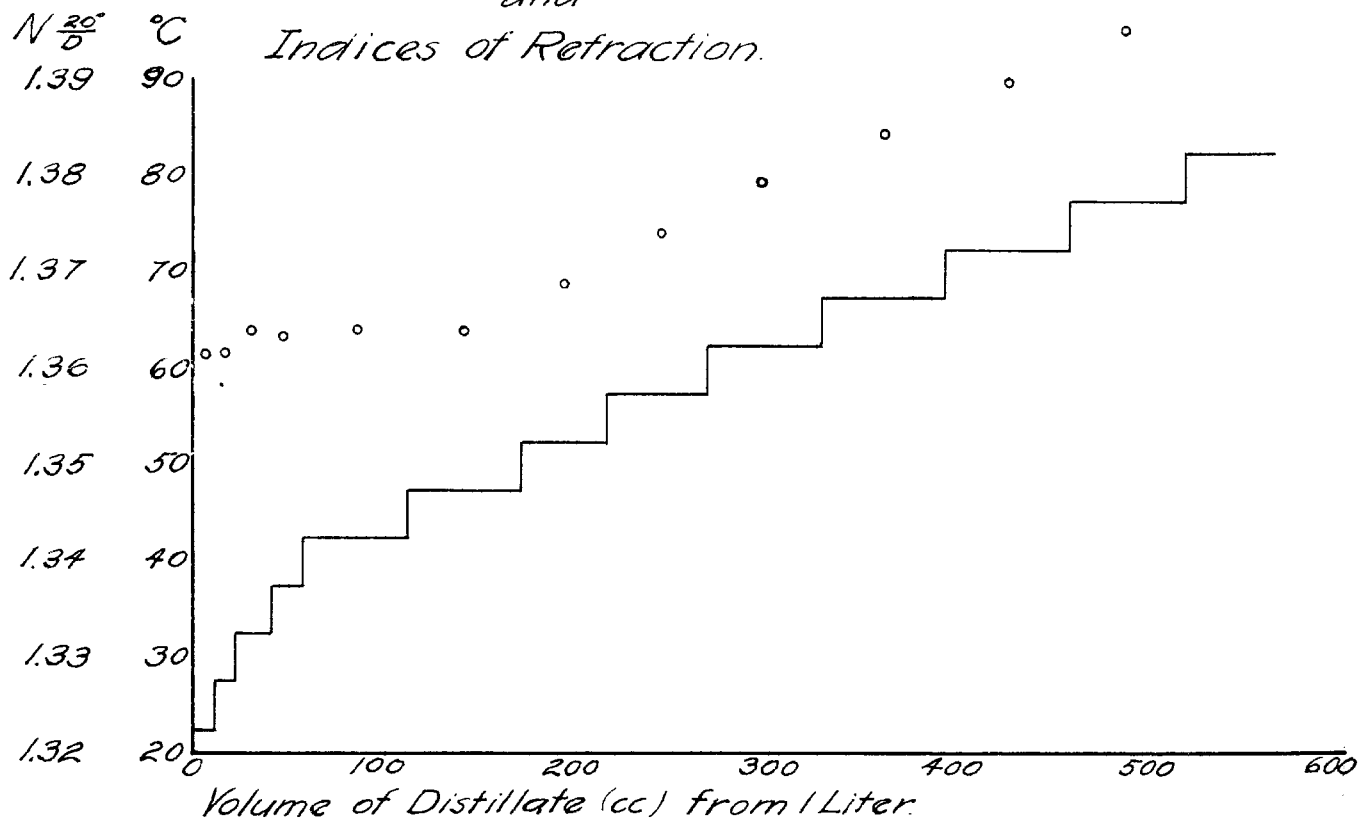
Orange Peel. The peel used was canned grated peel from the Exchange Orange Products Co. This consisted of the whole peel of the orange, grated to a pasty mass, and sterilized before sealing.

Methods of Analysis. Methods of analysis were desired for solutions of small amounts of benzol in orange oil, for small amounts of various fractions of gasoline in orange oil, for solutions of all concentrations of orange oil and gasoline, and also for the oil content of the peel.

*Curve I.*  
*Distillation Curve of Casing-head Gasoline.*



*Curve II*  
*Fractionation Curve of Casing-head Gasoline.*  
*and*  
*Indices of Refraction.*



The refractive index of benzol did not differ enough from that of orange oil to allow this property to be used as a basis for analysis. The refractive index of the oil changed from 1.4730 to 1.4731 for increase of benzol content from 0 to 2.66%. The optical rotation of orange oil is high so that this property can be used very satisfactorily. Curve III shows the relation between optical rotation,  $A_{5461}^{180}$ , 100 mm. tube, and the percent by weight of benzol.

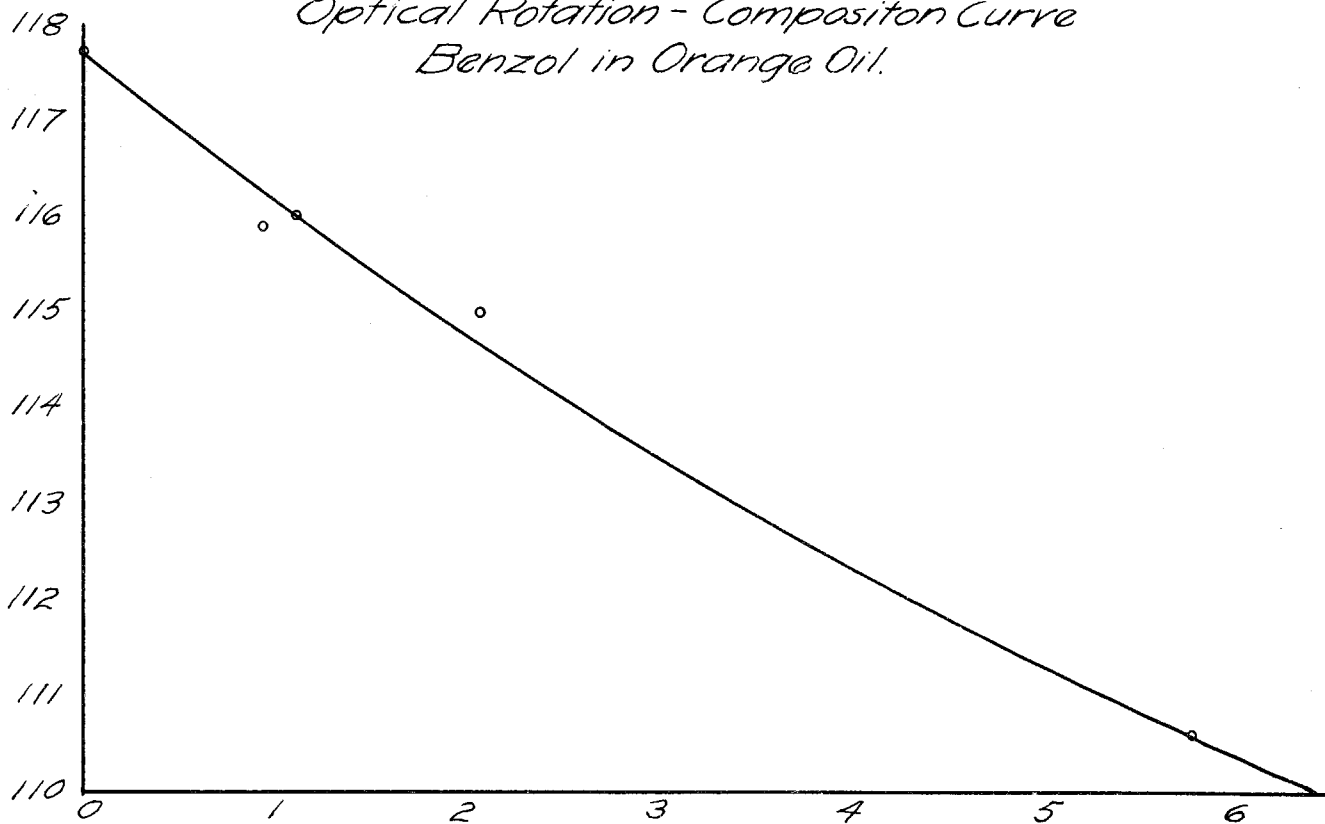
The refractive index of gasoline is low enough for this method to be used accurately and curve IV shows for three gasoline fractions the relation between the index of refraction and the percent by weight of gasoline.

Curve V (a) is similar to curve IV except that it covers the entire range of solutions for the special Union Oil fraction.

For analysis of the peel a Wiley extraction apparatus was first tried. The solution obtained by the extraction of a weighed amount of peel was analyzed by means of the refractive index and curve V (a) instead of the usual method of evaporating off the solvent. However this method has several disadvantages. Some of the lighter parts of the solvent may be lost during the extraction thus changing the refractive index of the solvent itself. The extracted oil has a different refractive index than expressed oil from which the curve was obtained. Also during the extraction some orange colored precipitate of some kind was formed which dissolved to some extent in expressed oil raising the refractive index. Pure expressed oil heated with gasoline under the same conditions did not give this precipitate. It is possible, considering the dark color and high refractive

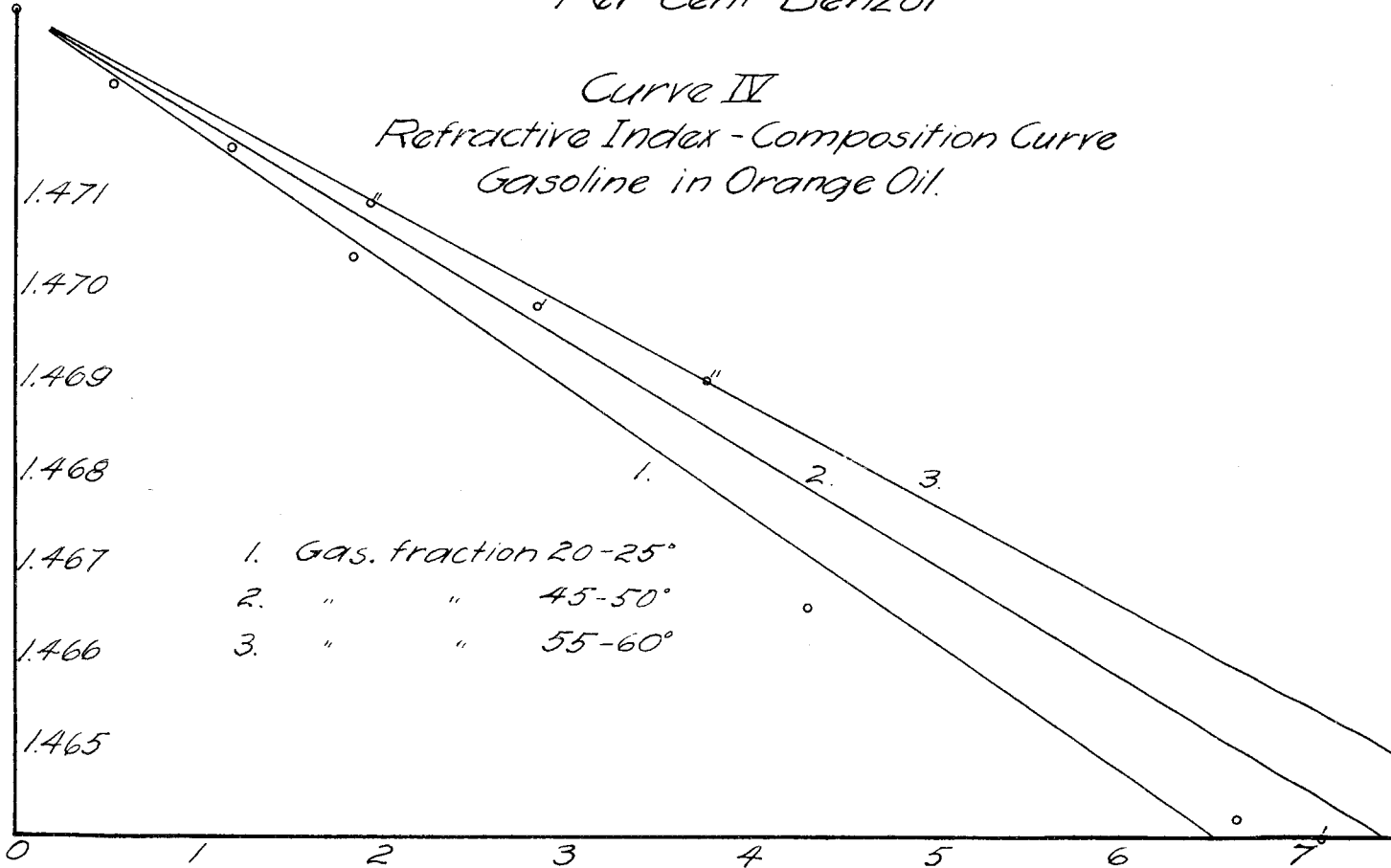
$A \frac{18}{5461}$

Curve III  
Optical Rotation - Composition Curve  
Benzol in Orange Oil.



$N \frac{20}{D}$

Curve IV  
Refractive Index - Composition Curve  
Gasoline in Orange Oil.



- 1. Gas. fraction 20-25°
- 2. " " 45-50°
- 3. " " 55-60°

Per Cent Gasoline.

index of this material, that it was some form of oleo resin. As a result of these disadvantages the extractive method of analysis was discarded and a modification of the method of Wilson and Young was used.<sup>1</sup> A weighed amount of peel was steam distilled and the distillate condensed in a nearly vertical condenser. The condensed water and oil drained down the condenser and the side of a burette. Under these conditions the oil collected in the burette was not emulsified with water and its volume could be accurately read. The water is taken from the bottom of the burette through an inverted siphon so that the level of the oil is kept at a convenient part of the burette. The distillation was continued until no more oil could be seen to condense. In order to determine the weight of oil from the volume the specific gravity had to be known. Wilson and Young advised in their article that this be determined for the oil in question. This was done by weighing a thin glass bulb of about 2.8 cc. capacity, first empty, then full of distilled water and finally of distilled oil at the room temperature. Two determinations gave the specific gravity as 0.845 at 22°. To obtain the weight of oil, then, the volume is multiplied by 0.845 and by 0.998 the density of water at 22°.

To analyze the peel after extraction some method had to be used which would take into account the presence of residual solvent which might distill over with the oil. If the volumes of orange oil and gasoline were exactly additive on mixing, weight percents could be converted to volume percents provided the densities of both substances were known. The specific gravity of expressed oil was determined by above method to be 0.846. The specific gravity of the gasoline (Union Oil fraction) was found by a Westphal balance to be 0.632. A mixture containing 84.0% by weight of

1 C. P. Wilson and C. O. Young J. I. E. C. 9 959 (1917)



*Curve I.*

*Concentration-Refractive Index Curve  
Orange Oil in Gasoline.*

1.47

1.46

1.45

1.44

1.43

1.42

1.41

1.40

1.39

1.38

1.37

0

10

20

30

40

50

60

70

80

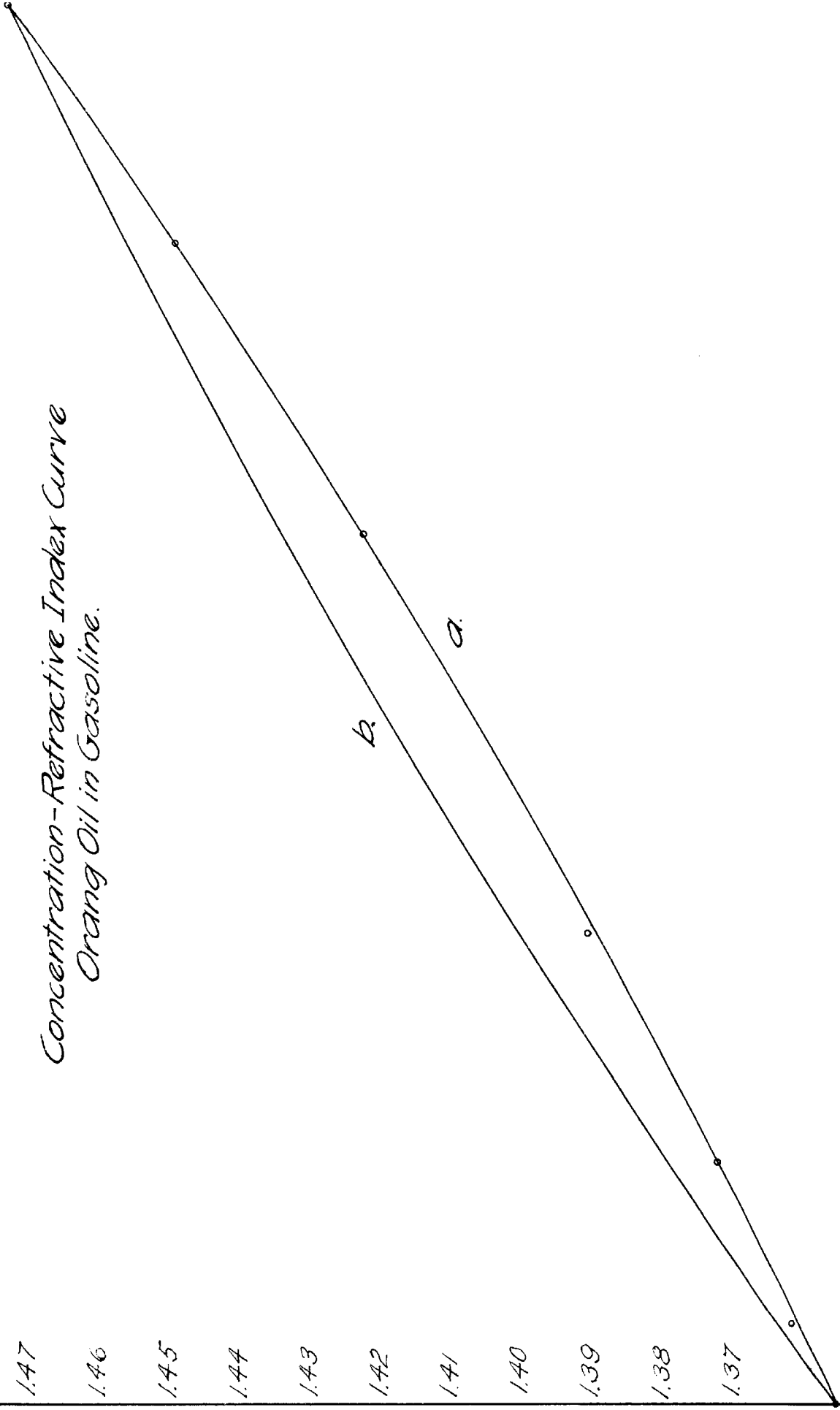
90

100

*b.*

*a.*

*Per Cent Orange Oil (a) by weight (b) by volume.*



at 22°, of 0.802 - while its calculated density expressed orange oil was found to have a density,  $\Delta$  on the basis of additive volume on mixing, is 0.801  $\frac{1}{2}$ . This indicated an inappreciable volume change on mixing so that weight per cents could be calculated over to volume per cents with a fair degree of accuracy. Using this result and the fact that the distilled oil has very nearly the same index of refraction as expressed oil, 1.4725 against 1.4730, curve V (b) was constructed from V (a). From the volume and index of refraction of the distillate the weight of pure distilled oil may be obtained from this curve and the specific gravity of distilled oil given above.

Removal of Solvent from the Oil. Benzol was the first solvent studied in these experiments. It has a comparatively high boiling point, 80° C, and if it were satisfactory any solvent having a lower boiling point would be satisfactory as regards volatility. After the bulk of the solvent is removed, at low temperature, under 50° C, there is no longer ebullition but simply evaporation from the surface. Therefore to have as rapid evaporation as possible a large surface should be provided. This was done by means of a roll of fine nickel gauze placed in the neck and bulb of a 200 cc. distilling flask, the gauze being kept wet by frequent shaking. The temperature used was 40° C, being in accordance with that used by Gibbs and Rosaria.<sup>1</sup> The pressure used was 80 mm, since this could be attained commercially. The following results were obtained for benzol.

1 Loc. cit.

Temp. 40° C                      Pressure 80 mm.

Time of heating	A <sup>18</sup> <sub>5461</sub>	% benzol
0 min.	111.7°	4.6
20	112.2	4.1
40	112.2	4.1
60	112.2	4.1

Temperatures raised to 50° C.

80	112.2	4.1
----	-------	-----

Temp. 40° C                      Pressure 50 mm.

Time of heating	A <sup>18</sup> <sub>5461</sub>	% benzol
0	110.3°	6.1
20	110.7	5.6
40	112.0	4.3
60	112.7	3.6
80	112.6	3.7

Heating pure orange oil under these conditions did not affect its refractive index but lowered the rotation from 117.7 to 116.3°. This change in rotation corresponds to about 0.9% benzol so that 3.2% (4.1 - .9) and 2.7% (3.6 - .9) are the corrected percentages of benzol remaining in orange oil after heating at 80 and 50 mm. respectively at 40° C.

The evaporation of gasoline fractions from orange oil was carried out in the same manner as for benzol with the following results.

Gasoline fraction, boiling range 20 - 25° C.

Temp. 40°. Pressure 80 mm.

Time of heating	N $\frac{20}{D}$	% gasoline
0	1.4695	2.6
20	1.4711	1.4
40	1.4719	0.8
60	1.4721	0.65
80	1.4724	0.4
100	1.4724	0.4

Gasoline fraction, boiling range 45 - 50° C.

Temp. 40° Pressure 80 mm.

Time of heating.	N $\frac{20}{D}$	% gasoline
0	1.4680	4.4
20	1.4700	2.6
40	1.4710	1.7
60	1.4715	1.3
80	1.4720	0.85
100	1.4721	0.75
120	1.4723	0.58
140	1.4723	0.58

Gasoline fraction, boiling range 55 - 60° C.

Temp. 40°. Pressure 80 mm.

Time of heating.	$N_{D}^{20}$	% gasoline.
0	1.4701	2.75
20	1.4711	1.75
40	1.4719	1.00
60	1.4720	0.90
80	1.4723	0.63
100	1.4723	0.63
120	1.4723	0.63

Extraction of Peel with Solvent. For these experiments the Union Oil fraction was used rather than those of smaller range since this type of fraction would be used in commercial operation. In using curve V (a) for analysis in these experiments some error was introduced owing to the different indices of refraction of solvent extracted oil and expressed oil for which the curve was constructed.

It was first desired to determine whether or not complete extraction could be obtained in a reasonable length of time with a moderate amount of solvent. For this purpose 100 gms. of peel was subjected to successive extractions of ten minutes duration each with 100 cc. portions of solvent. The peel was shaken with the solvent which was then poured off without squeezing. The following results were obtained extracting peel which was found by steam distillation to contain <sup>2.65</sup>~~2.65~~% oil.

Solvent portion	N $\frac{20}{D}$	% oil	Wgt. of solution	Wght. oil
1	1.3600	5.5	50.0 gm.	2.75 gm.
2	1.3570	2.5	60.5	1.51
3	1.3560	1.5	56.5	<u>0.85</u>
4	1.3555	0.0	58.5	Total 5.1
5	1.3555	0.0		

The results show that under these conditions the oil was completely extracted after three portions had been used. The total weight of oil extracted as indicated by the refractive index method is 5.1 against 2.65 gms. by steam distillation. The high result using the index of refraction was probably due to the larger amount of oleo resins being extracted which increased the refractive index.

To determine the effect of finer grating some peel was put through a food chopper three times. The resultant peel and some of the original were extracted under identical conditions and after twenty minutes the two solutions had the same indices of refraction.

In order to obtain some indication of the rate at which extraction takes place, a number of single extractions were made which were identical except for their durations. The results below are for the original grated peel and that reground in a food chopper using 25 gms. peel to 25 cc. solvent.

Duration in minutes.	Orig. grated peel.		Peel further ground.	
	N $\frac{20}{D}$	% oil	N $\frac{20}{D}$	% oil
5	1.3588	4.3	1.3589	4.3
10	1.3597	5.2	1.3597	5.2
15	1.3604	6.0	1.3604	6.0
20	1.3607	6.2	1.3607	6.2

The rate of extraction dropped off rapidly after about fifteen minutes.

Also the rates for the two peels were the same. The probably reason for this was that the peel was originally grated fine enough to break open all of the oil cells so that any finer division had no effect on the accessibility of the oil.

A two cell, counter current extraction was attempted but without much success owing to the large solvent loss. If 1, 2, 3, etc. are the portions of solvent going into the process and A, B, C, etc. are the charges of peel, the stages of the extraction will be,

C	D	E	F	
B	C	D	E	
(1 A)	(1 B)	1(2 C)	1 2(3 D)	
2	(2 A)	(3 B) A	(4 C) B A	etc.
3	3	4	5	
	4	5	6	

where the parentheses represent the extraction cells, the vertical columns represent the charges of peel and solvent going into the process and the horizontal rows those leaving it. The portion of solvent meeting a particular charge of peel was shaken with it and then poured off

and the remainder squeezed from the peel in a Buchner funnel by pressure and gentle suction. There was still a moderate amount of solvent retained in the peel and there was enormous loss due to evaporation as may be seen from the following results. The time of treatment in each cell was fifteen minutes, 100 gms. peel and 50 cc portions of solvent being used.

Orig. peel	2.65% oil
Charge C ( through both cells)	1.17% oil
Charge D ( through 1 cell)	1.70% oil

#### Solutions

leaving 1st. cell		Final solutions leaving 2nd. cell.		
No.	Wght. gms.	Wght gms.	% oil	Gms. oil.
1	16.0	6.5	45.5	3.0
2	18.0	8.0	35.6	2.9
3	16.0	5.0	46.5	2.3
4	16.5		% oil in 4	Gms. oil in 4
			12.3	2.0

Because of the large solvent loss the above results do not do the counter current method justice and accurate conclusions can not be drawn from them. If all the operations were carried on in a closed system by some suitable apparatus the results would undoubtedly appear much more favorable. A laboratory extraction cell for the purpose could be made from a short piece of large diameter pipe with caps for both ends. One cap is fitted at the center with a stuffing box and gland. A rod goes through the stuffing box which carries a perforated disk piston fitting the inside of the pipe. A small stop cock is also provided on the same cap. To operate, the other cap is removed and the charge of peel and solvent is



put in and the cap replaced. After extraction the peel is squeezed against the upper cap and the solution is taken out through the stop-cock.

Extracted Oil. Extracted oil was obtained by distilling off the solvent from two solutions of oil, the one prepared by successive extractions of 100 gms. peel with 100 cc. portions of solvent, and the solution resulting from the counter current extraction. The oil obtained in the first case, from dilute solution, was of much poorer grade as regards odor than the second which was obtained from concentrated solution. The latter oil compared quite favorably with expressed oil. The colors of the extracted oils were dark red whereas expressed oil is orange colored.

Acknowledgment is made for the kind cooperation of Dr. William N. Lacey of the Institute and Mr. C. P. Wilson of the Exchange Orange Products Co. and for the materials used in the investigation furnished by this company.

#### SUMMARY

Various phases of the process of solvent extraction of orange oil from the peel have been investigated.

It was found that high boiling solvents such as benzol could not be satisfactorily removed from orange oil by vacuum distillation. Lower boiling solvents such as light gasoline were removed to a satisfactory extent by this means.

The practicability of solvent extraction was demonstrated and the effects of time and degree of fineness were studied.