

## A COLORIMETRIC METHOD FOR THE DETERMINATION OF CITRAL IN EXTRACTS OF LEMON AND IN OIL OF LEMON.

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There have been various methods suggested and worked out for the assay of Citral in Extract of Lemon and for Oil of Lemon, gravimetric as well as colorimetric. Of the methods so far suggested, the Hydroxylamine, Fuchsin Sulphite, Sulphanilic Acid, Phenylhydrazine, Metaphenylenediamine methods, all seem to have some objectionable or uncertain features which make them not uniform in results in the hands of many operators.

The Fuchsin Sulphite method of Dr. Chace, (*Jour. Amer. Chem. Soc.*, 28, 1472, 1906), has received the most attention by chemists working with citral extracts.

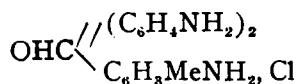
The Metaphenylenediamine method of Mr. Hiltner, (*Jour. Ind. & Eng. Chem*, 1906), which is generally preferred at the present time has good features for convenience and rapidity in manipulation, and can be conducted at room temperature.

As is well known to chemists working with citral, it possesses the characteristics of the aldehydes, and as it combines with phenylhydrazine, with ammonia and with hydroxylamine, upon these all colorimetric methods have been based. The following have been suggested:

The fuchsin sulphite reagent which was primarily used for the determination of acetaldehyde in alcohol, etc.; and metaphenylenediamine hydrochloride which is used in the fuchsin method for the decomposition of acetaldehyde in the alcohol used in the Chace method; therefore the two methods may give higher results in an extract of lemon containing acetaldehyde, which would be calculated as citral, while with the diaminophenol hydrochloride reagent only the citral is estimated, as this compound does not react with acetaldehyde and, as far as I have been able to determine, does not react with other compounds present in oil of lemon, except that in the presence of citronellal a violet coloration is produced proportionate to the amount of citronellal present. Of the various reagents suggested for the colorimetric estimation of citral aldehyde they bear a similarity in containing an "amino" group which combines with the citral.

In phenylhydrazine  $C_6H_5, NH_2, NH, HCl$  we have one amino and one imino radical.

In fuchsin



we have three amino groups.

In metaphenylenediamine hydrochloride,  $C_6H_4(NH_2)_2, 2HCl$  there are two amino groups.

In hydroxylamine hydrochloride,  $NH_2, OH, HCl$  there is one amino group while in diaminophenol hydrochloride,  $C_6H_3(NH_2)_2, OH, HCl$  there are two

amino groups, which appear to combine readily with citral and evidently form a definite compound, the product of which I have not fully worked out but have under investigation.

The following colorimetric method I have used for the past year in making Citral determinations parallel with other methods, with concordant results.

The method is of easy manipulation and can be conducted at room temperature:

*Reagent:* Dissolve .200 gram diaminophenol hydrochloride, (commercially known as Amidol) in 100 cc. of 65 percent by volume alcohol, preferably distilled over potassium hydroxide. The use of aldehyde-free alcohol does not seem to make any difference in the results, as acetaldehyde has no apparent effect upon the reagent. I find in making a large number of assays for citral the use of Mallinckrodt's recently distilled absolute alcohol to be sufficiently exact, as the reagent remains clear and colorless for several hours. The reagent is very readily soluble in 65 percent alcohol.

*Standard Citral Solution:* A solution of pure citral in fifty percent alcohol, containing .001 gram per cc.

*Solution of Extract of Lemon:* Weigh any quantity of the extract for examination, 15 or 25 grams, and dilute to 30 or 50 cc. with 50 percent alcohol, if a terpenless extract, making a 50 percent solution.

*Manipulation:* Similar to the Chace method, except that it can be conducted at room temperature.

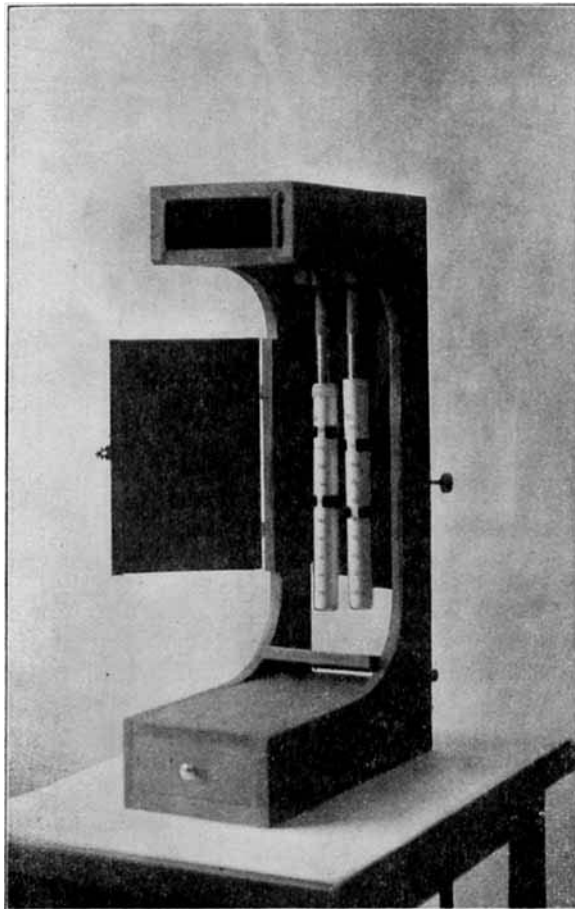
Place 2 cc. of the standard citral solution measured from an accurately graduated pipette, in a 250 mm. colorimeter tube, (using preferably an O. Schreiner colorimeter) add 20 cc. of 65 percent alcohol, and 15 cc. of diaminophenol reagent and make up to 50 cc. with 65 percent alcohol. Place 2 cc. of the extract in the other tube with 15 cc. of the reagent and make up to 50 cc. with 65 percent alcohol as before, mixing the contents of both tubes thoroughly and allowing both tubes to remain for 5 to 10 minutes at room temperature, when the maximum color is reached in both the citral tube and the extract under examination. The reading and calculation are made at once or a reading can be made at the expiration of fifteen or twenty minutes in duplicate. The calculation of percentage of citral content in the extract is made by placing the standard citral tube at the 30 mm. mark and adjusting the tube containing the extract under examination so that the two small disks of color as observed through the two immersion tubes are similar in tint.

Assuming that the extract tube was at 40, the calculation of percentage is made as follows:  $30 \times 2 \div 40 = 0.150\%$ .

The form of colorimeter which I have used is a modification of the O. Schreiner Colorimeter, which has some conveniences in manipulation over the ones obtainable from the instrument supply houses. The two immersion tubes are placed in the holders about 13/16 inch apart and adjusted parallel with each other, and the two mm. graduated tubes are attached to two movable slides at the back of the instrument, and movable upwards or downwards by a rack and pinion adjustment which moves them in a parallel position. In front of the

frame, covering the tubes while under observation, is a hinged front inclosing the tubes in a black box open at bottom, thus excluding all side lights or reflections.

The observation mirror at top instead of being made with a flat plane surface is divided in the center and mounted backwards at center, at an angle of about  $3^{\circ}$  or about  $1/12$  inch for each two -inch piece, making the mirror four inches in length, which converges the rays of light through the tubes and brings both images within the line of optical axis.



For the assay of oil of lemon the following is suggested as giving very good and comparative results. Dissolve 1 gram of the oil in sufficient 85% alcohol to make 20 cc. of solution and filter clear. Eighty-five percent alcohol will have about the same density as the oil. Make a 50% solution. Weigh out 15 grams and dilute to 30 cc. with 85% alcohol, or make a solution of 1 gram of the oil with sufficient 85% alcohol to make the volume 40 cc., and assay.

In the following tables I give the results of examination of both terpeneless extracts and extracts made from oil of lemon, covering a period of two years,

in parallel with Chace and the Hiltner methods and with diaminophenol hydrochloride:

		TABLE No. 1.		
		Chace Method.	Diaminophenol Method.	
No.	1	Ext. Lemon.....	.196	.196% citral
"	2	" .....	.187	.200
"	3	" .....	.176	.176
"	4	" .....	.187	.176
"	5	" .....	.166	.166
"	6	" .....	.181	.181
"	7	" .....	.227	.232
"	8	Concentrated		
"	9	Ext. Lemon.....	.830	.835
"	10	" .....	.785	.830
"	11	" .....	.880	.880
"	12	" .....	.704	.748
"	13	" .....	.875	.875
"	13	" .....	.790	.770

		TABLE No. 2.		
		Hiltner Method.	Diaminophenol Method.	
No.	1	Ext. Lemon.....	.176	.182% citral
"	2	" .....	.1304	.1428
"	3	" .....	.1668	.1714
"	4	" .....	.1578	.1578
"	5	" .....	.1394	.143
"	6	" .....	.105	.111

		TABLE No. 3.		
		Hiltner Method.	Diaminophenol Method.	
No.	1	Oil Lemon.....	4.20%	4.28%
"	2	" .....	4.00	4.14
"	3	" .....	4.28	4.28
"	4	" .....	3.16	3.14
"	5	" .....	4.61	4.68

While extreme accuracy is not claimed for the above method it is submitted with the hope that it may be of assistance to the pharmacist or chemist in making a comparative estimate of value or citral content of Extract of Lemon or Oil of Lemon for which it is given.

### THE DETECTION OF ADDED METHYL SALICYLATE.\*

WITH SPECIAL REFERENCE TO A NEW COLOR TEST AND THE CLAIM OF UNITED STATES GOVERNMENT CHEMISTS TO HAVE DEvised A METHOD.

The article which appeared in the Record of January, 1914, page 4, on the above subject has brought us so many inquiries and communications that we think it well to make further reference to the matter, especially as considerable interests are involved.

It will be recollected that it was claimed that the "specialists" of the Bureau of Chemistry are able to detect the addition of synthetically manufactured methyl salicylate in the natural product. We pointed out the importance of this, especially in view of the difficulties which previous workers had experienced in the task.

\*Reprinted from Perfumery and Essential Oil Record, Feb., 1914, p. 60.