

as above, it can be applied to Paris green containing free arsenious oxide and will give results which are strictly comparable with the Smith method. While this modification increases the time of carrying out the analysis on a single sample from about five to twenty minutes, it still results in a method which is much shorter than any known by the author for this class of compounds.

Now that the above modification has been worked out, it appears so simple and obvious that the author almost feels reluctant to publish it. When it is taken into consideration, however, that the Avery-Beans method has been before the Association of Official Agricultural Chemists for two years and that, although its limitations were spoken of, no one suggested the above change; that the author has also worked with the method for about two years without previously thinking of the change and that finally Avery and Beans, the originators of the method, did not suggest the above simple modification so that it might be applied to Paris green adulterated with arsenious oxide, it seems that the results are worthy of publication, especially since a shorter time and fewer manipulations are involved than in any other method for determining arsenious oxides in Paris green at present known to the author.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 87.]

A MODIFICATION OF THE BABCOCK-BLASDALE VISCOSITY TEST FOR OLIVE OIL.

BY HERBERT ABRAHAM.

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ACCORDING to Blasdale, Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap solution formed from a fixed amount of olive oil, saponified by a definite amount of potassium hydroxide, for detecting adulterated samples. At his suggestion Babcock, who had in 1886¹ examined a number of samples of butter and its principal adulterants, tested also a few of the most common fatty oils. His results show that butter gave the soap of lowest viscosity, and he also remarked that among the fatty oils, olive gave one of about the highest viscosity. The method was, at this time, used simply

¹ Reports N. Y. State Agricultural Experiment Station, 1886, p. 338; and 1887, p. 380.

for the examination of butter, and it was only in 1895 that Blasdale¹ applied it to olive oils. His paper contains the results obtained from a number of samples of pure and commercial olive oils, and also from a few oils which might be used as adulterants of olive oil. The figures obtained with different pure samples of olive oil varied considerably, but were always higher than those of the adulterated oils.

The method was considered especially promising for the detection of lard oil and as, at present, no good method is known by which the presence of the latter in olive oil can be determined with any degree of accuracy, its importance is obvious.

That this method has not come into more general use may be ascribed to the difficulty experienced in obtaining concordant results.

The writer has undertaken to study and, as far as possible, to mitigate or obviate the causes which led to the discrepancies in the method as hitherto carried out.

At first the method used by Blasdale² was strictly followed, but this was soon modified with respect to the means of determining the viscosity of the soap solution eventually obtained. Doolittle's viscosimeter³ was employed in the earlier tests, but the cost of this instrument has restricted its use to but a few laboratories. Moreover, for the present purpose there seems to be no theoretical advantage in measuring the viscosity by the torsion method, and no objection to the use of a viscosimeter which determines the rate of flow of the liquid through an aperture. In addition to being accurate, inexpensive, and easy of manipulation, it is important that the instrument used should be of such construction as to be readily kept at the desired temperature. Ostwald's viscosimeter⁴ appears to meet these requirements more satisfactorily than any other with which the writer is familiar, and it was thought that a comparison of this with the Doolittle viscosimeter might yield results of value. The following were obtained on testing aqueous solutions of sucrose.

¹ This Journal, 17, 937 (1895).

² Fifteen grams of oil are weighed in a saponification flask, and treated with 30 cc. of water containing exactly 7.5 grams potassium hydroxide, and 10 cc. of alcohol. This is heated on a water-bath until complete saponification has been effected. The resulting soap is washed into a large evaporating dish, heated until all the alcohol is expelled, and diluted to exactly 500 cc. at 15° C. The viscosity is determined by means of a torsion viscosimeter and calculated in terms of grams sugar per liter.

³ This Journal, 15, 173 (1893).

⁴ Ostwald-Luther: "Physico-Chemische Messungen," 2nd edition (1893), p. 266.

Grams sugar per liter.	Doolittle's viscosimeter.				Ostwald's viscosimeter.	
	I.		II.		III.	
	Retardation at 26.6° C.	Differ- ences.	Log. decrs. at 20° C.	Differ- ences.	Abs. viscosime- ter at 20° C.	Differ- ences.
0	6.7	..	255	..	100	..
100	7.1	0.4	295	40	132	32
200	7.5	0.4	345	50	186	54
300	8.0	0.5	410	65	306	120
400	8.9	0.9	500	90	455	149
500	11.0	2.1	670	170	712	257
600	14.5	3.5	1448	736
700	21.5	7.0
800	32.8	11.3
900	71.5	38.7

Column I gives the results expressed by the method employed by Doolittle, Column II by the method used by Babcock,¹ and Column III in terms of the absolute viscosity as will be used throughout the following work.

It will be noted that Columns I and III are obtained directly from the readings, while the results in Column II have been increased without rendering them more accurate, by obtaining the logarithmic decrements and then multiplying by 10,000. In spite of this, however, the ranges between the consecutive figures in Column III are greater than those in the other two columns. Ostwald's viscosimeter is, therefore, quite as delicate as Doolittle's. It costs about forty cents, whereas the Doolittle viscosimeter is sold for \$65. Moreover, Ostwald's instrument requires for a test only about one-hundredth as much of the liquid, and, on account of its smaller size, it is easier to maintain at the desired temperature throughout the operation.

The changes which next suggested themselves were (1) the avoidance of transferring the soap from one vessel to another, and (2) the use of a smaller bulk of soap solution.

Both were effected by employing one-fifth the quantities of oil, potassium hydroxide,² and of alcohol used by Blasdale. This corresponds to a soap solution of 100 cc.

As the results of considerable study of the details of manipulation, it was found that the principal causes of variable results obtained by the method are (1) variations in the amount of

¹ Report N. Y. State Agricultural Experiment Station for 1886, p. 316; also *J. Anal. Chem.* (1887), 1, 151.

² This amount was subsequently diminished slightly in order to obtain more concordant results.

caustic potash present in excess; (2) incomplete expulsion of the alcohol used in saponification; (3) absorption of carbon dioxide by the excess of alkali, during the expulsion of the alcohol; (4) varying the temperature at which the actual viscosity is determined; (5) varying the dilution of the soap solution.

Each of these points was studied separately with a view of finding the best conditions of manipulation.

Varying the Amount of Potassium Hydroxide Used.—It was found that the viscosity of the soap solutions increased rapidly with the amount of potassium hydroxide present in excess of that

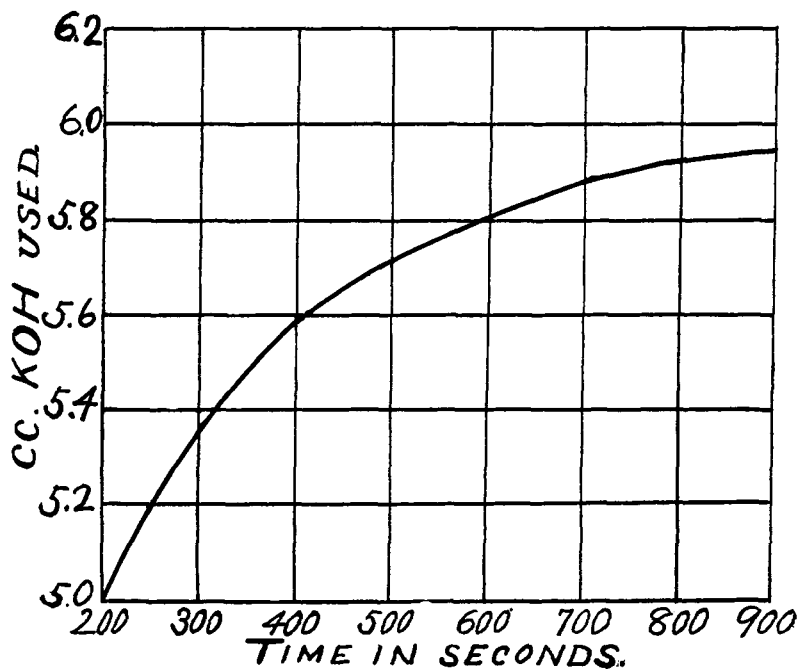


Fig. 1.

required for saponification. Thus, with an olive oil, saponified with 5 cc.¹ potassium hydroxide, the average time of flow was 200 seconds; with 5.2 cc., 253 seconds; with 5.4 cc., 310 seconds; with 5.6 cc., 412 seconds; with 5.8 cc., 568 seconds; with 6 cc., the soap was too viscous to test to any degree of accuracy.

These results are plotted in the form of a curve (Fig. 1). It is evident from these experiments that relatively small variations

¹ One cc. containing $\frac{1}{4}$ gram exactly.

in the amount of free alkali present cause large changes in the viscosity of the solution. Even the variations due to the differences in the Koettstorfer figure of different samples may seriously affect the results. It is much better, therefore, instead of using a *fixed amount* of alkali in each case, to determine the alkali required for the saponification of each sample, and then vary the amount of alkali taken so that the soap solution to be tested will always contain a *fixed excess* of potassium hydroxide.

Expelling the Alcohol Completely with "Ordinary Air."—The same oil saponified with 4.80 cc. potassium hydroxide (2.50 cc. in excess of that required for saponification) etc., and the alcohol expelled completely by a current of air passed over the surface of the liquid, gave an average time of flow of 148 seconds.

Expelling the Alcohol Completely with "Ordinary Air" as above, Followed by Passing in Carbon Dioxide (Converting all the Caustic into Carbonate).—The same oil under this treatment gave an increase of 93 seconds in the time of flow, while the soap solution of another oil, whose original time of flow was 137.2 seconds, was increased by nearly 23.8 seconds.

These and other irregularities led to the conclusion that the use of carbon dioxide is unsatisfactory.

Expelling the Alcohol Completely with Air Free from Carbon Dioxide.—The same oil saponified as above, and having a stream of pure air passed over its surface for half an hour while being heated on a water-bath, gave an average time of flow of 151.6 seconds.

This led to the adoption of air free from carbon dioxide.

Length of Time Required to Expel the Alcohol.—Saponification as above with a Kroonig valve in fifteen minutes, the viscosity being determined directly without expelling the alcohol, gave an average time of flow of 143 seconds.

Another portion saponified in fifteen minutes, with air free from carbon dioxide passed through for fifteen minutes, gave an average time of flow of 150.4 seconds.

A third portion saponified as above, air free from carbon dioxide being passed in for ten minutes, gave an average time of flow of 15.2 seconds.

Ten minutes was, therefore, considered sufficient for the removal of the alcohol.

Varying the Temperature.—Saponified with 4.80 cc. potassium hydroxide, etc., in fifteen minutes, air free from carbon dioxide being then passed in for ten minutes. When the soap solution was tested at 15° C., the time of flow was 205.3 seconds; at 16° C., 196.0 seconds; at 17° C., 185.0 seconds; at 18° C., 172.7 seconds; at 19° C., 161.3 seconds; at 20° C., 150.4 seconds; at 21° C., 142.0 seconds; at 22° C., 134.3 seconds; at 23° C., 127.0 seconds; at 24° C., 120.0 seconds; at 25° C., 114.0 seconds.

The results are plotted in a curve (Fig. 2).

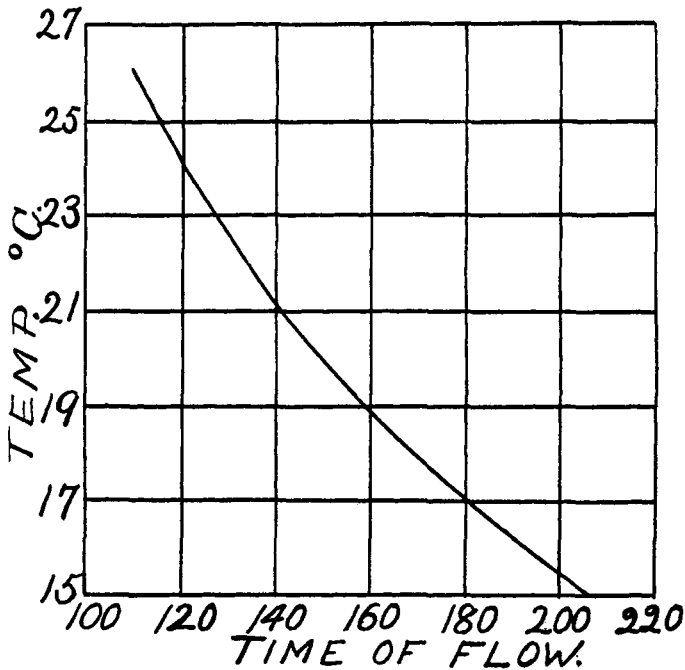


Fig. 2.

Varying the Dilution of the Soap Solution.—The average time of flow of a certain soap solution was 161 seconds; the same, three-quarters strength, was 120 seconds; one-half strength, 105 seconds; one-quarter strength, 98 seconds; for water alone, 95 seconds. The results are plotted in Fig. 3.

In order to avoid or minimize any variations arising from the above conditions, and to obtain a solution of such a viscosity as to permit of convenient and accurate measurement, the following details should be observed:

(1) In every case add exactly 2.5 cc. of potassium hydroxide (0.25 gram per cubic centimeter) in excess of that required for saponification. This amount is desirable as it gives a comparatively low viscosity, offering the following advantages: (a) It takes less time to flow, reducing the total time of the method; (b) the soap dissolves more easily; (c) the results are more uniform and are just as accurate.

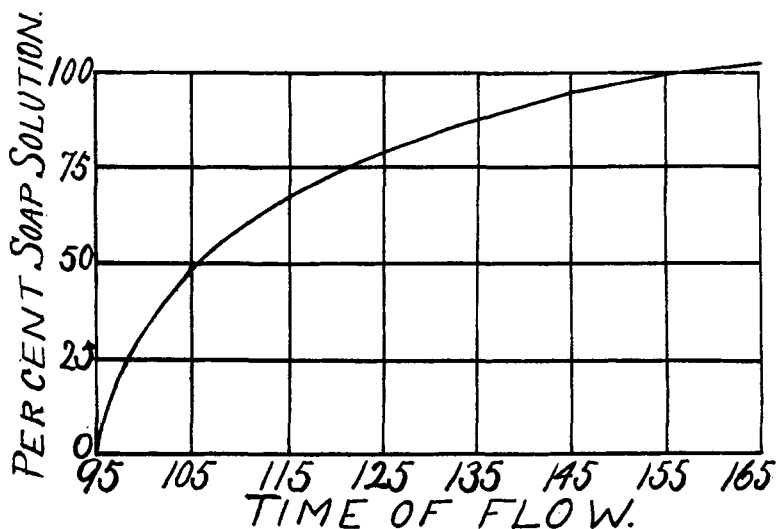


Fig. 3.

(2) Two cc. of alcohol are chosen as being the minimum amount to secure rapid saponification.

(3) The alcohol should be expelled completely by means of a stream of air, free from carbon dioxide, passed through the flask for about ten minutes. This secures the greatest accuracy combined with the greatest rapidity.

(4) The soap should be diluted to 100 cc. in conformity with the above conditions.

(5) The viscosity should be determined at *exactly* 20° C.

THE METHOD AS FINALLY ADOPTED.

I. *Apparatus.*—(a) 100 cc. flasks accurately calibrated and thoroughly cleansed and dried; (b) a “water-suction apparatus” capable of raising a column of mercury at least 300 mm.; (c) a 5 cc. measuring pipette, graduated accurately to $\frac{1}{20}$ cc. for measuring out the potassium hydroxide solution. The end of this

pipette should be drawn out into a thin-walled capillary so as to decrease the size of the drops and thus render the delivery more accurate. The diameter of the capillary should be such that 60 to 65 drops of the potassium hydroxide solution are delivered per cubic centimeter;¹ (*d*) a stopper with a Kroonig valve to fit the 100 cc. flasks, used while saponifying. This permits any vapors to escape, but does not allow air to enter the flask, thus avoiding contamination by carbon dioxide; (*e*) a ring-stand carrying a water-bath and U-tubes to remove carbon dioxide from the air used; (*f*) an Ostwald viscosimeter and accessories.

II. Reagents—(*a*) A solution of potassium hydroxide containing *exactly* 0.25 gram per cubic centimeter, made up accurately by titration; (*b*) alcohol practically free from impurities, used in titrating. This should be tested for acidity and neutralized, if necessary; (*c*) a solution of phenolphthaleïn, 1 gram per liter in pure alcohol; (*d*) ether for washing out the viscosimeter, pipettes, etc.; (*e*) standard hydrochloric acid approximately N/5.

III. Determination.—Weigh out two portions of exactly 3 grams of the oil into 100 cc. flasks, care being taken not to introduce any on the necks of the flasks.

Determination of the Amount of Potassium Hydroxide Required for Saponification.—To one portion add 5 cc. potassium hydroxide and 2 cc. alcohol from their respective pipettes. Adjust the seal and heat on the water-bath for from ten to fifteen minutes, when the saponification should have taken place. Rinse the soap into a beaker with about 100 cc. pure alcohol, add 10 to 12 drops phenolphthaleïn, and titrate with hydrochloric acid. Calculate the amount of potassium hydroxide to be added next time in order that there shall be 2.5 cc. in excess of that required for saponification.

Preparing the Soap Solution.—To the second portion of oil, add the calculated amount of potassium hydroxide, and 2 cc. alcohol. Adjust the seal and saponify on the water-bath. The time required for saponification may be materially reduced by occasionally twirling the contents of the flask. If thus agitated at intervals, it rarely takes longer than ten minutes. After saponification, the seal is replaced by a stopper carrying two tubes, a short one and

¹ The pipette used by the writer was calibrated by weighing the water which it delivered at 20° C.; when 5 cc. were delivered altogether the accuracy was $\pm \frac{1}{100}$ cc., while the greatest error for any individual cubic centimeter was $\frac{1}{70}$ cc.

a long one, drawn out so as to come about 5 to 10 mm. above the surface of the liquid. The lower end of the longer tube is curved upwards so as to present the mechanical carrying off of the liquid. The other end of this tube is connected with the suction, while the shorter tube is connected with the absorption train. By placing the finger over the entrance to the last U-tube, a partial vacuum is created in the flask, and the evaporation of water and alcohol is accelerated, as is seen by the frothing of the soap. The finger is removed, and the operation repeated once or twice at intervals. The evaporation should not be carried so far as to remove the water present, else the soap will solidify and take an inconveniently long time for its subsequent solution. It will suffice to take the soap down to the consistency of molasses (which requires five to ten minutes). Without allowing it to cool, the flask is filled about half full of boiling water. Upon rotating, the soap should go into solution in a minute or two. The flask is now immersed in a stream of cold water until it attains about the temperature of the room, when it is diluted to the mark with cold, distilled water and mixed well by shaking.

Finding the Viscosity.—The viscosimeter should be cleaned by attaching it to suction and running first alcohol and then ether through it: it is then immersed in a cylinder filled with water kept *exactly* at 20° C.

Great care must be exercised on introducing the 3 cc. of soap solution into the viscosimeter, and, on sucking it up the capillary (which must be done very slowly), because if it once becomes frothy, it will be almost impossible to secure a satisfactory reading. With a little practice in manipulation, however, the soap can be maintained free from enclosed bubbles during the entire operation. The first reading is usually rejected so as to give the liquid a chance to assume the temperature of the surrounding water-jacket. Five or more closely agreeing readings should be averaged to obtain the time of flow. The readings should agree within two seconds. The instrument is first calibrated by using pure, distilled water which should take in the neighborhood of 100 seconds to flow through. Since the instruments are made of capillary tubes of different diameters, one should be selected which takes about 100 seconds with water—this being most satisfactory for the method.

The "absolute viscosity" is calculated by means of the following formula:

$$v_1 = \left(\frac{s_1}{t} \right) t_1,$$

where t_1 = the time of flow,

s_1 = the specific gravity of the liquid under consideration,
and t = the time of flow of water under like conditions.

The specific gravities of the soap solutions of all the principal oils, as based on a large number of determinations, were found to approximate 1.07 (within ± 0.005), so that this figure may be substituted in place of s_1 in the above expression. An extreme error of 0.005, due to this assumption, will merely affect v_1 by 0.5 to 0.7.

The formula, therefore, reduces to

$$v_1 = kt_1,$$

where k is a constant for the particular apparatus employed. The value of v_1 for pure, fresh olive oil of good quality is usually 165-185, for most other oils it is about 125-135.

In general, it is advisable to determine the viscosity of the soap solution while fresh, as it has been found that after standing several days the viscosity is sometimes increased and sometimes decreased.

In the hands of the writer, the time required for a determination by the present method is less than half that required by the method as described by Blasdale.

In conjunction with Dr. H. C. Sherman, at whose suggestion this investigation was undertaken, the modified method has been applied to a number of samples of olive, lard, and other fatty oils, in comparison with the "constants" by means of which such oils are usually judged. The results of this study will be given in a subsequent paper.

QUANTITATIVE LABORATORY,
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THE VISCOSITY OF THE SOAP SOLUTION AS A FACTOR IN OIL ANALYSIS.

BY H. C. SHERMAN AND HERBERT ABRAHAM.

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AS PART of a comparative study, undertaken in this laboratory, of some of the so-called analytical constants, we have determined