for the true heat of bromination, the apparatus could be worked in the same way as it was standardized, using oil and bromine in place of sulfuric acid and water. This should give results which are accurate to perhaps 1 or 2 per cent. This should make also a convenient apparatus for certain student calorimetric work where it could well be used in place of larger and more expensive types of calorimeters.

It might be noted, too, that the stirring must be vigorous in the large calorimeter. Several types of stirrers were tried inside of the mixing chamber and a spiral form was finally adopted as being the most efficient for this purpose.

CONCLUSIONS

I—A special apparatus and a method for the determination of the true heat of bromination have been proposed and tried.

II—A new apparatus on the same principle has been proposed for the quick determination of specific heat but it could well be used for other purposes, such as the determination of heat of neutralization, the Maumené number in terms of calories per gram of oil, etc.

III—The heats of bromination in calories per gram of oil have been determined on a number of oils and these values compared with the iodine numbers.

IV—It has been shown that the heat of bromination is not directly comparable to the iodine number, and the reason why such an agreement could not be expected has been pointed out.

V—The heats of solution of bromine and most oils in carbon tetrachloride have been shown to be very small.

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OPTICAL DISPERSION OF CHINESE WOOD OIL AS AN INDEX OF PURITY

By E. E. WARE

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The peculiar properties exhibited by Chinese wood oil have led to the development of some interesting methods of examination for the detection of adulteration. In practically all cases, although the property upon which the individual method is based is characteristic enough to warrant its use as the basis of a method of examination, difficulties have arisen in the control of the conditions of operation, in consequence of which different laboratories report widely varying results.

The two methods offered by Ware and Schumann,¹ one of which depends upon the insolubility of the sodium soap of elaeomargaric acid in absolute alcohol, and the other upon the insolubility of the light-converted elaeostearic acid glyceride in high gravity petroleum ether, produce accurate results when operated under properly controlled conditions of temperature and concentration; but they do not seem adapted to the use of the factory control laboratory.

The heat test as modified by Committee D-1, Subcommittee III, of the American Society for Testing Materials,² is a logical method of analysis, inasmuch as it depends for its accuracy upon the careful observation of the progress of a gelatination which is

characteristic of this oil, and upon which is dependent the development of such varnishes as contain it. The report of the committee, submitted as a result of a series of tests carried out by different operators upon accurately prepared samples, shows that the method must be carefully handled to produce closely agreeing results, and that under ordinary circumstances it should not be relied upon to detect adulteration under 5 per cent.

The iodine jelly test, as investigated by the same committee, seems but little better. However, as mentioned in an earlier paper,¹ the gelatination of wood oil by iodine in chloroform solution is subject to a marked retardation by the presence of small amounts of alcohol. This fact may explain some of the variations in results, as the different operators were not using chloroform from the same source, and no doubt some of the chloroform might have contained traces of alcohol.

The index of refraction of wood oil, as has been pointed out by various investigators, is considerably higher than that of other drying and semi-drying oils. All attempts to calibrate, for analytical use, the variations in refractive index, due to mixing other oils with wood oil, have been unsuccessful in establishing the use of the refractometer in the quantitative estimation of adulteration. In this method

FIG. 1

the temperature correction factor is large enough to make possible an error of one per cent for every degree variation in temperature control. There exists also the difficulty of making an exact setting of the cross hairs of the reading telescope upon the dividing line between the illuminated and the dark fields. This difficulty is quite pronounced when using white light as a source of illumination, for the line of division between the fields is not sharp, even after a careful adjustment of the compensator, to correct for dispersion.

E. C. Holton² noticed, when working with the Abbé direct reading refractometer, that the rotation of the prism required for correct compensation for wood oil and for other oils is very different. He has gathered together considerable unpublished data in an attempt to calibrate this difference in compensator reading to a point where he can make use of it as an analytical method.

Brier³ takes advantage of this property of abnor-

¹ THIS JOURNAL, 6 (1914), 806.

² Proc. Am. Soc. Test. Mat., 1915, p. 204.

³ THIS JOURNAL, 7 (1915), 571.

² Private communication.

³ THIS JOURNAL, 7 (1915), 953.

mally wide dispersion exhibited by wood oil, in a method in which he demonstrates that when using a Pulfrich refractometer equipped with a prism whose relative dispersion is not large, the compensation offered by the secondary prism made up of oil is sufficient to produce an effect of anomalous dispersion. The compensation by other oils will narrow the spectrum but will not reverse it.

Inasmuch as this compensation offered by the secondary oil prism is due to the natural dispersion of the oil, it is possible to simplify the examination by

FIG. II

making a direct reading of this dispersion uninfluenced by the dispersion of any other medium. This may be accomplished by using as the refracting medium a hollow prism filled with the oil to be examined.

The most convenient instrument for the measurement of such relative dispersion is the ordinary spectrometer equipped with an autocollimating eyepiece. Fig. I shows such an instrument in use in this laboratory.

If light of a definite wave length be focused on the small totally reflecting prism in the eyepiece of the telescope, it is reflected through the slit and the objective lens, from which it enters the oil prism as parallel rays. After becoming refracted by the oil, it is reflected from the silvered rear face of the prism and refracted back along its original path to the slit from which it came. The angle through which the table of the spectrometer must be rotated to properly focus the slit image upon the slit itself, is the angle from which, knowing the angle of the prism, may be computed the refractive index for that particular wave length, according to the formula

$$\mu = \frac{\sin \frac{1}{2} (A + D)}{\sin \frac{1}{2} A},$$

where $\frac{1}{2} D$ is the angle of rotation of the table minus the angle of the prism. If, instead of using a monochromatic source of light, we use a source emitting light of several wave lengths, we may, by making settings on the several bright lines characteristic of the source of light, measure the indices of refraction for the several wave lengths, and express the relative dispersion for any two of them according to the general formula

$$\frac{\mu_c - \mu_F}{\mu_c - 1},$$

in which μ_c is the index of refraction for light of wave length 0.65629 and μ_F for wave length 0.48614. In order to get a maximum value for the relative dispersion angle the author made use of a brass electrode arc lamp as a source of light. This light gives characteristic bright lines in both the red and the blue, with several other lines in the green and the yellow. Fig.

II gives some idea of the spectrum from the brass arc after dispersion by wood oil. The lines marked are the ones used for the measurements reported. They persist without adsorption by any of the oils used.

The angles D_1 , D_2 and D_3 , from which are computed the refractive indices for lines 1, 2 and 3, vary with the nature of the oil, with the temperature, and according to the angle of the prism; but for the same oil in a definite prism they are constant for a fixed temperature. The difference $D_2 - D_1$ is just as accurately a measure of the relative dispersion for an individual prism as is the difference between the corresponding refractive indices. This fact simplifies the procedure of the method, for the fine adjustment of the spectrometer has sufficient range to permit the reading of the angular difference $D_2 - D_1$ without resetting the spectrometer circle. The vernier of the instrument illustrated has a least reading of 6" with a possibility of interpolation to one second.

The dispersion or angular difference for wood oil as measured while confined in a hollow prism of angle $20^\circ 1'$ is $26' 54''$, while for soya bean oil for the same temperature it is $12' 54''$, or expressed in vernier units of 6' each, it is 269 and 129, respectively.

As is shown in Table I and Fig. III, the dispersion of wood oil adulterated with varying percentages of

FIG. III

soya bean oil may be expressed quite accurately by a straight line, if we select, as coördinates, percentage adulteration and angular dispersion. This curve

will be reasonably accurate for other adulterants, for although there may be some variation between the dispersions of the various adulterating oils, when used with wood oil to 15 per cent or less, the differences in their effects upon the dispersion of the wood oil is relatively small. This fact may be better appreciated by comparing the two curves of Fig. III, which start from somewhat different points but lack little of being coincident at the lower ends, representing adulterations up to and including 15 per cent.

The temperature correction for the angle of dispersion is quite small, about one second per degree Centigrade, which, figured in percentage adulteration, is 0.1 per cent. This is very considerably less than the correction on the index of refraction. The angle D_3 reading of Table I shows something of the effect

Oil No.	Per cent wood oil	Adulterant oil	Angle $D_2 - D_1/2$	Angle D_3	Vernier units	Apparent adulteration Per cent	Error
1	100		26' 54"	22° 37' 48"	269		
2	100		26' 54"	22° 36' 12"	269		
3	100		26' 48"	22° 34' 24"	268		
4	100		26' 42"	22° 35' 24"	267	1.5	
5	95	Soya	26' 6"	22° 30' 36"	261	5.5	0.5
6	95	Soya	26' 12"	22° 30' 24"	262	5.0	
7	95	Linseed	26' 12"	22° 30' 48"	262	5.0	
8	90	Soya	25' 24"	22° 23' 12"	254	10.7	0.7
9	90	Linseed	25' 30"	22° 26' 24"	255	10.0	
10	90	Soya	25' 36"	22° 24' 48"	256	9.3	-0.7
11	85	Soya	24' 48"	22° 19' 48"	248	15.0	
12	75	Soya	23' 24"	22° 8' 48"	234	25.0	
13	60	Soya	21' 18"	21° 48' 40"	213	40.0	
14	40	Soya	18' 30"	21° 25' 48"	185	60.0	
15	25	Soya	16' 24"	21° 6' 48"	164	75.0	
16	15	Soya	14' 54"	20° 56' 36"	149	85.7	0.7
17	10	Soya	14' 12"	20° 48' 24"	142	90.7	0.7
18	5	Soya	13' 36"	20° 43' 36"	136	95.0	
19	0	Soya	12' 54"	20° 36' 54"	129	100.0	
20	0	Tallow seed	14' 18"	21° 3' 48"	143		
21	0	Sesame	12' 42"	20° 29' 12"	127		
22	0	Rape	12' 48"	20° 29'	129		
23	0	Linseed	13' 42"	20° 55' 36"	137		

No. 1—Am. Soc. for Test. Mat. 1915: Pure Wood Oil

No. 2—Gillispie and Sons: Pure Wood Oil

No. 3—Acme White Lead and Color Works: Pure Wood Oil

No. 4—Acme White Lead and Color Works: Rejected shipment

Nos. 6, 7, 9 and 10—Am. Soc. for Test. Mat. 1915

of variation in temperature. Although precautions were taken to maintain the temperature constant throughout the work, slight variations were unavoidable, and each slight variation made a big change in angles D_1 , D_2 and D_3 , although the effect upon $D_2 - D_1$ was relatively small. If it were possible to equip a spectrometer with a satisfactory constant temperature device, it is very probable that the variations in angle D , due to added impurity, would make a satisfactory means of detecting adulteration. The advantage gained by the measurement of this angle by the spectrometer rather than by the ordinary refractometer would be in the greater accuracy in reading.

The method of examination of wood oil by measuring its dispersion should appeal to the factory chemist. The individual readings may be made rapidly; there are no computations involved; the apparatus is not expensive nor difficult to keep in adjustment, and the accuracy of the method compares very favorably with that of any other in use at the present time.

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THE NEPHELOMETRIC DETERMINATION OF SMALL AMOUNTS OF ESSENTIAL OILS

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The two general methods most commonly employed for determining essential oils in such food products as extracts and cordials are: (1) extraction of the oil with a suitable solvent, and (2) precipitation of the oil and measurement of its volume after collection by centrifugal force. These methods give results much too low with very small amounts of oil, because both of the appreciable loss of oil during the evaporation of the solvent and of the proportion of oil which does not separate by centrifugal action.

The fact that an alcoholic solution of most essential oils will form a cloudy emulsion on the addition of water suggested the possibility of using the degree of turbidity as a measure of the quantity of oil present.

The emulsion formed consists of a large number of tiny oil globules which are capable of reflecting light. The number of globules and hence the amount of light reflected is evidently dependent on the amount of oil present. It remains, then, only to find some method of measuring the amount of light reflected, and by comparison with a standard containing a known weight of oil, a method is available for determining the amount of oil in an unknown sample.

APPARATUS

The simplest instrument which suggested itself for this purpose was the well known candle turbidimeter. This, however, was not found suitable for use with translucent precipitates like oil emulsions because the light passes through the globules and makes the end point obscure and inaccurate.

It was therefore necessary to use a nephelometer, the form actually employed being that devised by Kober.¹ The basis of the instrument is the well-known Duboscq colorimeter, in which the length of column of liquid is varied by moving two glass plungers up or down by means of thumb screws on the back of the instrument. The length of each column is indicated on a scale by a pointer which moves up and down with the plunger.

To convert the colorimeter into a nephelometer, it is necessary:

1—To paint the sides of the plungers with black asphaltum paint, leaving the ends clean and with sharply defined edges. The black coating prevents any reflections entering the plunger except through the bottom. (This change may be permanent as it does not interfere with the use of the instrument as a colorimeter.)

2—To arrange a shield which will surround the tubes and by a central partition prevent any reflection from one to the other. Two apertures are made in the shield directly in front of the tubes and the only way in which light can reach the tubes is through these openings.

3—To enclose the eyepiece with a box into which the head may fit comfortably. This prevents reflections on the eyepiece.

¹ J. Biol. Chem., XIII, 4, 485; J. Am. Chem. Soc., 35 (1913), 1585.