Determination of the Total Unsaturation of Tung Oil by Catalytic Hydrogenation[1,2]

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METHODS for the determination of unsaturation of tung oil and modified tung oils have generally been based on halogenation. Such methods (3, 7, 15, 19), and proposed modifications (1, 6, 13, 16) thereof, while giving results indicative of the total unsaturation under a specified set of conditions (time of contact, excess of reagent, temperature, and catalyst) are at best empirical as applied to tung oil or other triene conjugated substances. The inadequacies of the various halogenation methods for measuring conjugated unsaturation have been commented upon by various workers (2, 5, 8, 11, 12).

The iodine values for the total unsaturation of tung oil reported in the literature and obtained by a variety of methods range from 217 to 266. Even after allowing for variation of the tung oils of diverse and unknown origins this spread in values is greater than might be expected and probably reflects the difficulty of measuring conjugated unsaturation by means of the empirical methods generally applied for this purpose.

Hydrogenation as a means of determining conjugated unsaturation possesses obvious advantages over halogenation since there is no possibility of substitution occurring, and the reaction proceeds to completion. However methods based on hydrogenation have never attained wide application because they generally have required the use of more complicated apparatus than have methods of halogenation.

Waterman, de Kok, and van Vlodrop (17) used the method of van Westen (18) to measure total unsaturation in tung oil. The apparatus used with this method was designed primarily for relatively volatile substances. Jordan (9) employed a simpler volumetric method in which the sample and catalyst were dispersed in ethyl acetate. Kaufmann and Baltes (10) used a similar apparatus to determine the total unsaturation in essang *(Ricinodendron africanum)* oil which, like tung oil, contains glycerides of eleostearic acid. These workers dispersed the oil in glacial acetic acid and used a platinum-silica gel catalyst. More recently, Ogg and Cooper (14) and Hellman and Senti (4) have used quantitative hydrogenation as an analytical tool.

The present authors have applied to tung oil a modification of the technique and apparatus developed[4] by the Naval Stores Research Division of the Bureau of Agricultural and Industrial Chemistry for the quantitative hydrogenation of terpenes and related compounds. The apparatus (Figure 1) comprises essentially a gas burette, manometer, reaction flask, magnetic stirrer, water bath, and electric heater. The hydrogenation is carried out in glacial acetic acid with the aid of a platinum catalyst. The amount of hydrogen absorbed by the substance, expressed in iodine value units, is a quantitative measure of the total unsaturation. Hydrogen absorption expressed in this manner has been designated by Waterman, *et al.* (17) as the hydrogen iodine value of a substance.

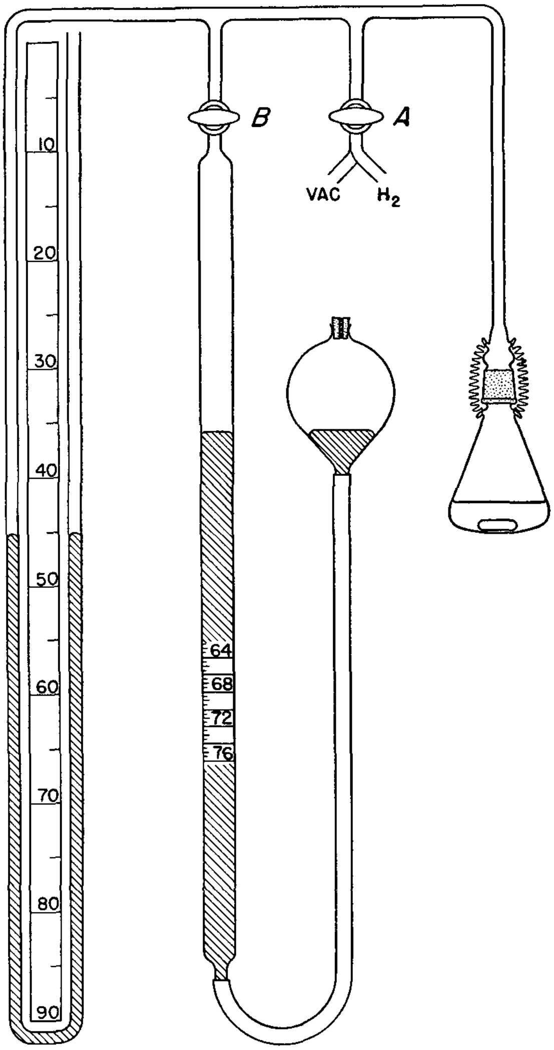

FIG. 1. Apparatus for analytical hydrogenation. Apparatus consists of 100-ml. gas burette, open end manometer, 125 ml. reaction flask with 19/38 ₮ joint, and stopcocks (spring loaded and gas-tight under both vacuum and pressure) interconnected as indicated by means of 2-mm. bore capillary tubing.

Procedure

Twenty-five ± 0.5 mg. of platinum oxide is weighed onto aluminum foil and transferred to the reaction flask. Twenty ml. of glacial acetic acid is added by pipette. The sample (0.2 to 0.3 g.) weighed to 0.1 mg. is then introduced by means of a weighing pipette and the reaction flask secured with tension springs to the body of the apparatus. The apparatus except the gas burette, is alternately evacuated and filled with hydrogen through cock A (Figure 1). The flush-

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[1] A report of a study made under the Research and Marketing Act of 1946.

[2] Presented at the 25th Fall Meeting of the American Oil Chemists' Society, Chicago, Illinois, October 8-10, 1951.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[4] Unpublished procedure.

ing operation is repeated three times. Following the final flushing, the gas burette is filled with hydrogen through cock B. The system is now closed by crossing cock A and equalized with respect to atmospheric pressure with the leveling bulb of the gas burette.

The initial temperature, pressure, and volume is read, the reaction flask surrounded with a water bath, the time noted, and the magnetic stirrer started. The water bath is brought quickly to 60°C. and held at this temperature throughout the reaction. It is essential that the temperature be maintained at this value in order to insure the complete solubility of the sample and its hydrogenated derivatives throughout the period of reaction.

A positive hydrogen pressure of approximately 120 mm. is maintained in the system during hydrogenation. After one hour, or at the cessation of pressure and volume change, stirring is stopped, the water bath is removed from the reaction flask, and the system is allowed to cool to ambient temperature. One hour is usually sufficient for this purpose. When equilibrium is attained, the final temperature, pressure, and volume are read.

The volume of hydrogen absorbed is converted to standard conditions of temperature and pressure, corrected for the blank (run in an identical manner except for the addition of the sample), and then converted to equivalent iodine absorption by means of the following equation:

$$\text{Hydrogen iodine value} = (V_1 - V_2)\ 25384/22412 \cdot \text{wt. of sample}$$

where V_1 is the ml. of hydrogen absorbed at S.T.P., V_2 is the ml. of hydrogen absorbed by blank at S,T.P., 25384 is twice the atomic weight of iodine × 100, and 22412 is the volume in milliliters of 1 mol. of hydrogen under standard conditions.

Application of the Method

The method described above has been applied to the determination of the total unsaturation in more than 100 samples of acids, esters, and oils, containing conjugated and/or unconjugated double bonds. Hydrogen iodine values for a number of such substances are shown in Table I. Each value represents the average of at least two determinations.

Inspection of these data shows that in the case of substances containing only nonconjugated double bonds there is good agreement between the hydrogen iodine and Wijs iodine values, but only the hydrogen iodine value affords a quantitative measure of the total unsaturation of those substances containing conjugated double bonds.

The reliability of the method with respect to completion of the hydrogenation can be readily checked by a rapid iodine value (Wijs) determination made on the catalyst-free residue following the determination of a hydrogen iodine value. This practice should be followed whenever unfamiliar material is analytically hydrogenated.

Summary

The use of catalytic hydrogenation as a quantitative method for the measurement of total unsaturation in tung oil and related products containing conjugated unsaturation, has been investigated.

The apparatus, which comprises essentially a gas burette, manometer, and reaction vessel, is relatively simple, is constructed entirely of glass, and employs an externally mounted magnetic agitator. The weighed sample and platinum catalyst are suspended in glacial acetic acid during hydrogenation. In the case of tung oil and partially hydrogenated tung oil, heating of the reaction vessel is necessary to complete the hydrogenation.

Hydrogen iodine values representing the total unsaturation in domestic and imported oils, alpha- and beta-eleostearic acids, the residual unsaturation in partially hydrogenated tung oils, and the unsaturation of other organic materials are reported. Tung oil and eleostearic acid gave hydrogen iodine values of approximately 240 and 271, respectively.

Analytical hydrogenation, as described, is particularly well suited for the determination of unsaturation in conjugated systems.

TABLE I

Hydrogen Iodine Values of Various Conjugated and Unconjugated Unsaturated Substances

Substance	Hydrogen iodine value	Wijs iodine value[a]	Theoretical iodine value
Maleic acid	217.6		218.8
Dimethyl maleate	176.3		176.3
Dimethyl fumarate	176.8		176.3
Methyl linoleate (70%)	121.1	120.8	
Methyl linoleate (96%)	166.9	166.5	
Peanut oil methyl esters	93.1	92.0	
Eleostearic acid, alpha	271.2	188.0	273.8
Eleostearic acid, beta	270.9	186.7	273.8
Tung oil, Chinese	228.2	164.3	
Tung oil, Uruguayan	225.0	163.5	
Tung oil, domestic	238.8-241.1[b]	165.7	
Tung oil, domestic	239.0[c]	165.7	
Tung oil, domestic	239.8	165.7	
Hydrogenated, No. 1[d]	207.2	150.2	
No. 2	188.3	137.4	
No. 3	172.6	128.8	
No. 4	152.6	119.7	
No. 5	152.1	118.9	
No. 6	149.9	118.9	
No. 7	148.9	118.9	
No. 8	148.0	120.1	
No. 9	147.6	118.8	
No. 10	146.4	117.4	
No. 11	142.8	116.2	
No. 12	139.8	112.6	

[a] ASTM method D555-47.

[b] Maximum and minimum values for 7 determinations.

[c] Amyl acetate used as solvent and the reaction carried out at room temperature; volume of blanks is excessive with this solvent.

[d] Numbers refer to samples of the same tung oil hydrogenated under different conditions of temperature and pressure.

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