

Improved Apparatus and Methods for Quantitative Hydrogenation

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THE authors have previously described an analytical hydrogenation technique for measuring the total unsaturation in tung oil, partially hydrogenated tung oil, and the eleostearic acids (4). The apparatus comprised the usual gas measuring apparatus, manometer, and reaction flask in conventional arrangement. Total volume of hydrogen gas absorbed, corrected to S-T-P and corrected additionally for the volume of hydrogen taken up by the catalyst and solvent, was used to calculate the unsaturation of the material being hydrogenated in terms of iodine (Iodine Value).

Constant use of this method in our laboratory has inevitably made apparent the need for certain modifications of both apparatus and procedure. It is the purpose of this paper to describe the improved apparatus and procedure.

The redesigned apparatus features a gas-holding and measuring section free from stopcocks and moving joints. Its gas-tight integrity is consequently easy to maintain. A device for the delayed addition of the material being hydrogenated has been built into the apparatus so that, when desirable, the solvent-catalyst system can be reduced prior to reduction of the sample. Trouble-free, uninterrupted agitation within the reaction flask during hydrogenation has been assured by modification of the flask and of the magnetic stirring bars. Operation of the redesigned apparatus is essentially that of conventional gas-measuring apparatus with one exception. A leveling bulb altered to serve the additional purpose of a gas valve has been incorporated.

Apparatus

Erlenmeyer flasks of 125 ml. capacity, fitted with 24/40 outer joints and hooks for tension spring fasteners and bowed outward slightly at the bottom (Figure 1-R), have proved to be excellent reaction vessels. The slight downward bow of the flask bottom insures constant centering of the magnetic stirring bar and this in turn guarantees uninterrupted agitation during the hydrogenation.

Alnico² bar magnets, glass-encased, are excellent but fragile instruments for obtaining agitation within the reaction flasks. Teflon-covered² magnets usually have the cover composed of two or more pieces (*i.e.*, a central cylindrical section with end plugs). Incipient leakage past the end plugs of the cover is aggravated by the requisite alternate application of vacuum and pressure at the beginning of hydrogenation procedure. Glass-encased Alnico² bar magnets provided with protective tips (Figure 1-S) made from Teflon tubing are both durable and efficient.

The hydrogenation procedure described previously (4) involves concurrent reduction of the platinum oxide catalyst and the sample with subsequent correc-

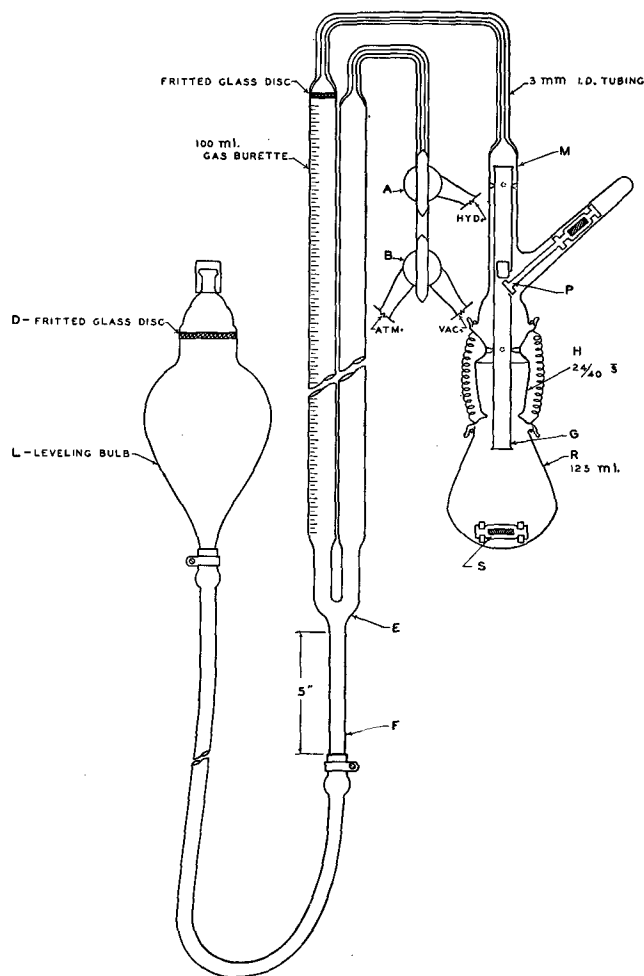


FIG. 1

tion of the total volume of gas consumed by means of a blank determination carried out with catalyst and solvent only. It is desirable in certain catalyst-solvent systems where the blank determinations tend to lack consistency to be able to divorce the volume of hydrogen consumed by the catalyst and solvent from the volume of hydrogen taken up by the sample. The sample-introducing-device (Figure 1-M) of Mason (2) is well suited to this purpose.

The apparatus (Figure 1) is simple and compact, with the gas burette (graduated to 0.1 ml.) doubling in function as one arm of a manometer, as in the apparatus described by Noller and Barusch (3). The only possible location where gas leakage might occur is the joint between the reaction flask and the main body of the apparatus. Leakage there is quite improbable because the joint is stationary. The ultimate gas holding and measuring portion of the new apparatus is devoid of stopcocks.

The fritted glass disc at the top of the gas burette is for the purpose of preventing finely divided parti-

¹One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

²The mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

cles of mercury from being swept over into the reaction flask during the flushing and filling operation.

The leveling bulb (Figure 1-L) was designed to eliminate, at point (F), a stopcock with its attendant leakage, lubrication, and mercury contamination troubles. The fritted disc (D) must be of fine porosity to prevent passage of mercury in either direction. Enough mercury is added above the disc so that when the leveling bulb is upright, a layer of mercury completely covers the upper surface of the fritted disc, thereby blocking air passage. Tilting the bulb slightly uncovers a portion of the upper surface of the fritted disc (D), thus allowing passage of air. The operation of the leveling bulb is thus that of a simple gas valve. The volume of the leveling bulb and its flexible connecting tubing must at least equal the combined volume of the gas burette and the adjacent, inter-connecting manometer arm.

Temperatures are read from a thermometer hanging alongside the gas burette.

Operating Procedure

Before placing the micro-beaker containing the sample in the sample-introducing device (M) and before attaching the reaction flask containing the solvent, stirring bar, and catalyst to the apparatus, tilt the leveling bulb (to allow passage of air through the fritted disc) and lower it, thus draining all mercury out of the main body of the apparatus down to a point three inches or more below (E) and simultaneously filling *completely* the leveling bulb. Restore leveling bulb to upright position, thereby blocking passage of air by covering the upper surface of the fritted disc with mercury and thus permitting vacuum to be applied to the system. Sweep the apparatus with air to remove any residual hydrogen from a previous run by opening stopcock (A) to (B) and (B) to vacuum. After the apparatus has been swept with air, place the micro-beaker containing the weighed sample in the sample-introducing-device. This is conveniently accomplished by inserting the micro-beaker into the guide tube (G) and pushing it up past the magnetically activated plunger tip (P) by means of a small rod. Lubricate joint (H) well and secure the reaction flask with its contents (stirring bar, solvent, and catalyst) to the apparatus with tension springs. With stopcock (B) open to vacuum, alternately evacuate and fill the system with hydrogen at 3 to 5 p.s.i. gauge pressure through stopcock (A). Repeat the flushing operation (this should be done rapidly) three times. After the final filling of the apparatus with hydrogen, close stopcock (B), open stopcock (A) to (B), and tilt the leveling bulb to allow air passage through the fritted disc. All subsequent operations are performed with the leveling bulb open to the atmosphere. Open stopcock (B) carefully to vacuum and draw excess hydrogen gas out of the apparatus until the level of the mercury in the tube (E-F') is about one inch above the level of the mercury in the leveling bulb. Close vacuum and elevate the leveling bulb until mercury rises past the Y-junction of the two arms and traps gas in the graduated arm of the apparatus. Open stopcock (B) to the atmosphere and equalize the mercury levels in the two arms by manipulating the leveling bulb and then make the initial P-V-T readings.

If the blank for the solvent-catalyst system being used is known, add the sample immediately. For max-

imum precision, the series of operations, flushing, filling with hydrogen, and initial volume reading should be done in a uniform manner. Carry out the hydrogenation under slight positive hydrogen pressure (about 100 mm. of Hg) and continue until the gas volume is stabilized or changes by less than 0.1 ml. in 10 minutes. Make the final reading of P-V-T and the requisite calculations. If the magnetic stirrer used heats during operation, a short equilibrating period (15 minutes) should precede the final P-V-T readings.

If the blank is not known, start the stirrer but delay addition of the sample until the catalyst and solvent have taken up their quota of hydrogen (as indicated by constant volume readings or changes of 0.1 ml. or less over a 10-minute interval) at which time make the initial P-V-T readings, drop the sample, and conduct the hydrogenation as before. All volume readings are, of course, made with the stirrer stopped.

If ambient temperature or pressure changes occur prior to final volume reading, the changes should be compensated for by altering appropriately (as proposed by Joshel [1]) the pressure imposed on the system.

Solvents for Use in Analytical Hydrogenation Procedures

The sparing solubility of tung oil and the products of tung oil hydrogenation in glacial acetic acid at room temperature led to the investigation of other possible solvents, to the end that the hydrogenation might be carried out at room temperature and the time-consuming heating and subsequent cooling to ambient temperature be avoided.

Pure *n*-alkyl esters of mono basic aliphatic acids, used in conjunction with a 10% palladium-on-carbon catalyst, were found most suitable. The use of 10% palladium-on-carbon catalyst was adopted because of the excessive blanks encountered when platinum oxide was used with these esters.

The aliphatic esters, as a group, satisfy most of the requirements for a suitable hydrogenation solvent. These are: a) good solvency at room temperature for tung oil and its hydrogenation products, b) no adverse effects upon the activity of the catalyst, c) reasonably low volatility and, d) low viscosity. Butyl propionate, available with good purity from the Eastman Company,² has been used successfully in our laboratory for the hydrogenation of tung oil, the eleostearic acids and related materials. The blank (volume of hydrogen consumed by solvent and catalyst alone) for 25.0 ml. of *n*-butyl propionate and 25.0 mg. of 10% palladium-on-carbon is quite low (*i.e.*, 6 to 8 ml. of hydrogen at S-T-P) and the hydrogenation of 0.2-0.3 g. samples of tung oil can be completed at room temperature in less than one hour. The butyl propionate may be recovered by distillation under reduced pressure after filtering off the catalyst. The recovered ester has a somewhat lower blank (3 to 4 ml.).

Shortening the time required to complete hydrogenation improves precision by reducing the possibility of wide fluctuations in temperature or pressure between initial and final volume readings.

Summary

Improved apparatus and techniques for the measurement of olefinic unsaturation by quantitative hydrogenation are described. These involve use of Mason's sample-introducing device, of *n*-alkyl esters of mono-basic fatty acids as solvents, and of palla-

dium-carbon catalysts, thereby speeding up the determinations, improving their precision, and extending their utility.

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A Rapid Dielectric Method for Determining the Oil Content of Flaxseed¹

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THE theory and application of high-frequency oscillators to chemical analysis was covered in a previous paper (1). Briefly summarized, the basic principle in the application of high-frequency oscillators to chemical analysis depends upon the fact that when a solution or solid is placed within the coil or between condenser plates of a high-frequency oscillator, it affects the characteristics of that oscillator to an extent determined by the nature and concentration of the sample. Any one or more of the characteristics or their changes, such as plate or grid current, plate or grid voltage, or frequency changes may be measured. The addition of the sample to the coil or condenser produces changes in frequency in

accordance with the formula: $f = \frac{1}{2\pi \sqrt{LC}}$

where f = frequency

L = inductance of the oscillator coil

C = capacitance of the parallel resonant circuit

The electronic tester described in the previous paper functions on the principle that the radio frequency impedance of a condenser is changed when the properties of the dielectric between the plates are altered. The test cell condenser is designed to hold liquids. At the beginning of a test the cell is empty, and the dielectric between the cylinders of the cell is air. When an oil solvent is poured into the test cell, the impedance is lowered and the frequency of the oscillator is changed. The change in frequency is indicated on the frequency meter. When a small quantity of oil is added to the solvent, the impedance is raised. If more oil is added to the solvent, there is a further change in the dielectric value and a corresponding increase in the impedance of the test cell condenser. Impedance changes shift the frequency of the oscillator circuit and are indicated on the frequency meter.

The previous paper covered in detail the equipment and procedure for determining the oil content of soybeans by a dielectric method. The purpose of the present paper is to describe the modifications in the procedure that are necessary to adapt the dielectric

The Application of High-Frequency Oscillators to Analysis of Flaxseed for Oil Content

Briefly, the dielectric method for determining the oil content of flaxseed and soybeans consists of simultaneously grinding and extracting the sample in a Stein Laboratory Mill (Figure 1)² in the presence of orthodichlorobenzene, filtering, and then measuring in the Steinlite LOS Unit (Figure 2)² the dielectric value of the filtrate and converting this value to percentage of oil.

The major difficulty faced in adapting the method to flaxseed was in the filtering. The flaxseed-orthodichlorobenzene mixture, after simultaneously grinding and extracting with the mill, was a gelatinous mixture that required from 30 minutes to several hours to filter. This occurred regardless of the moisture content of the flaxseed. Vacuum filtering and pressure filtering, using many different types of filter paper, were tried without appreciably reducing the filtering time. As a similar filtering difficulty with wet soybeans was resolved by heating the samples for five minutes with infrared radiant heat (1), tests were made to determine the effect of infrared radiant heat on flaxseed. It was found that such heating of flaxseed for 4 minutes—regardless of original moisture—would prevent the formation of a gelatinous mixture during the grinding operation and the filtering time was reduced to 6 to 8 minutes per sample.

Since a current of air blowing over the sample was also necessary to carry off the released moisture and to help keep the surface of the samples cool and thereby lessen the danger of scorching, a special infrared, forced-draft, drying unit was designed and built (Figure 3). This unit consists of two Chromalox² type RAD, 800-watt infrared radiant heaters mounted parallel on adjustable rods in a cabinet that has a perforated metal floor and a blower unit designed to blow air up through the floor. The heaters can be adjusted to any height up to 10 inches above the samples. The height used for flaxseed and soy-

¹The study on which these findings are based was made under authority of the Agricultural Marketing Act of 1946 (RMA, Title II).

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