A Rapid Method for the Determination of Oil in Tung Fruit*

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THE TUNG OIL industry needs a rapid, yet accurate, procedure whereby tung fruit arriving at the mill and ground tung kernels being processed in the mill can be analyzed for oil content. In our endeavor to develop such a method, we have tried to use inexpensive laboratory equipment and to limit the manipulations as far as possible without sacrificing accuracy. It is our belief that this method, with slight variation in the technique and with suitable density-oil curves, could be utilized on other oil seeds. Therefore, this method will probably be of interest to workers in other fields of vegetable oil technology.

The principles of this method are quite simple, and well known. A weighed portion of ground tung kernels are reground with an accurately measured portion of a high-density solvent of low vapor pressure. The solution of oil in the solvent is filtered off, and its density determined by means of a picnometer. Reference to a density-per cent tung oil curve or table gives the per cent of tung oil in this solution. The per cent of tung oil in the tung kernels and tung fruit is then calculated from an appropriate equation.

Acetylene tetrabromide, the solvent used in this procedure, was chosen because of its excellent oil-solvent properties, high density, low water solubility, and low volatility at room temperature. The density of the acetylene tetrabromide (s-tetrabromoethane) is adjusted to 2.933 at 25° C., if it is not that already. This is done by adding acetylene tetrachloride, if its density is too high, or an especially pure grade of acetylene tetrabromide if its density is too low. However, a manufacturer of this solvent has offered to supply it at the required density.

The acetylene tetrabromide is added to the ground tung kernels from a five-milliliter pipette. This pipette must be accurately calibrated as to the weight of acetylene tetrabromide that it will deliver at the temperature to be used. If the room temperature is close to 25° C., the solvent may be brought to that temperature in a constant temperature bath before pipetting, so that the same weight of solvent may be used in all the determinations. However, if the room temperature is considerably higher or lower than 25° C., it is necessary to pipette the solvent at room temperature. Particular attention must be paid to the draining of the pipette during calibration and when used in a determination. This should be done for a definite time to be determined by allowing it to drain, without touching the tip to the liquid or to the side of the mortar, until there is a marked time interval between drops. This was between twenty and thirty seconds after the steady flow of solvent from the tip of the pipette had ceased.

It was found impossible to grind tung kernels fine enough in a mill to permit the complete removal of the oil by the solvent. Therefore, it is necessary to thoroughly regrind the ground tung kernels with sand in a mortar, and then triturate the ground kernels and sand with the added solvent. The necessity of regrinding the tung kernels with sand in the mortar limited the size of the sample of tung kernels to the amount used.

The two-milliliter Gay-Lussac specific gravity bottles used do not lend themselves readily to density determinations at 25° C. if the room temperature is appreciably higher than this temperature. Therefore, the density of the tung oil-acetylene tetrabromide solution is determined at room temperature, and the per cent of tung oil in this solution is taken from the appropriate density-per cent tung oil curve, such curves having been prepared for the various temperatures encountered in practice.

In the preparation of these density-per cent tung oil curves, standard tung oil-acetylene tetrabromide solutions containing 14, 15, 16, 17, 18 and 19 per cent of tung oil were prepared, and the densities of these solutions were determined at 20, 25, 30 and 35 degrees Centigrade. The per cent of tung oil was then plotted against the determined densities for each temperature and appropriate curves were drawn. By interpolation, similar curves were drawn for the intervening temperatures. Experiment showed that these interpolated values were in good agreement with determined values.

METHOD

The laboratory sample of 25 or 100 fruits is weighed and carefully separated into hulls, shells and kernels. The separated components are weighed and the percentage of each is calculated. The undried tung kernels are ground twice in a "Russwin" food grinder, type No. 1, using the sixteen-tooth cutter. The ground kernels are thoroughly mixed and a five-gram sample of the ground kernels is accurately weighed on an analytical balance sensitive to at least 1 mg. The weighed sample is transferred to a four-inch mortar; two grams of fine sea sand, reagent grade, is added and the contents are ground with a pestle until intimately mixed. Five milliliters of acetylene tetrabromide is added with a pipette which has been carefully calibrated as to the weight of acetylene tetrabromide that it delivers, and the tung kernels are then triturated vigorously with the acetylene tetrabromide and sand for five minutes. The mixture is then allowed to stand for ten minutes, after which the trituration is repeated.

A 65-mm. accurate 60°-angle funnel is fitted by a cork into a one-inch Pyrex test tube having a side arm for suction. A 25-mm. perforated porcelain filtering disc is placed in the funnel and a 27-mm. filter paper is cut and placed on the disc. Suction is applied at the side arm of the test tube, a water pump provided with a suitable trap being a satisfactory source of vacuum.

The triturated tung kernel-solvent mixture is poured on the filter paper and the solution is filtered off with suction. The density of the filtered solution is determined at room temperature in a two-milliliter Gay-Lussac specific gravity bottle which has been carefully standardized as to volume.

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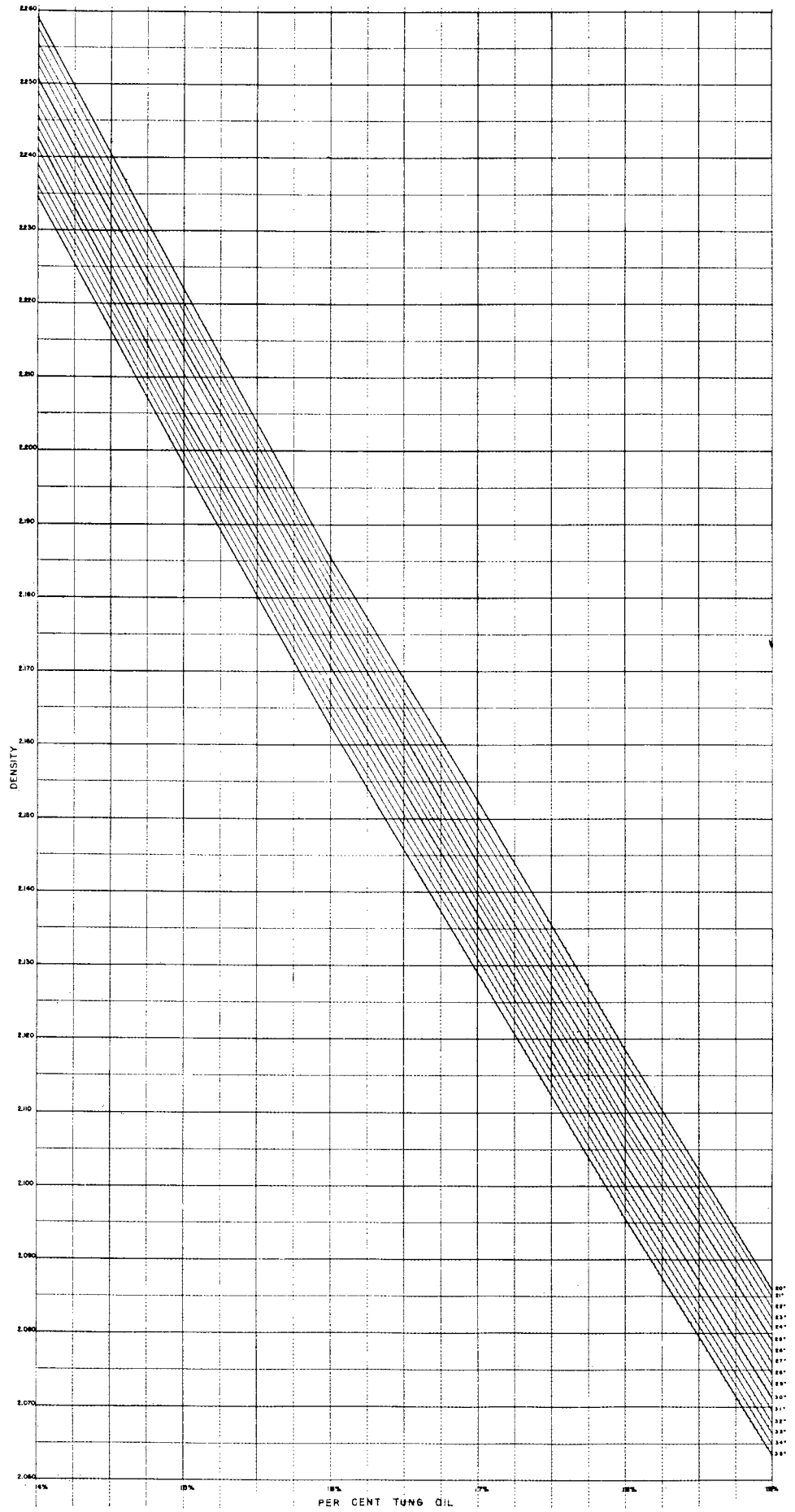
DENSITY
PER CENT TUNG OIL

DENSITY MEASUREMENTS OF TUNG OIL—ACETYLENE TETRABROMIDE SOLUTIONS

% Tung Oil	DENSITY AT 20° C.	25° C.	30° C.	35° C.
0	2.9445	2.9335	2.9242	2.9124
14	2.2600	2.2520	2.2439	2.2359
15	2.2235	2.2154	2.2074	2.1996
16	2.1878	2.1800	2.1721	2.1543
17	2.1536	2.1456	2.1388	2.1305
18	2.1197	2.1123	2.1049	2.0973
19	2.0872	2.0799	2.0725	2.0651
20	2.0560	2.0489	2.0417	2.0343
100	0.9380	0.9349	0.9315	0.9282

EXAMPLE

Assuming that the density of the tung oil solution is 2.104 at 25° C., it is found, by reference to the density-per cent tung oil curve for 25° C., that this solution contains 18.40 per cent tung oil, and X (per cent tung oil in kernels) =

$$\frac{0.1840 \times 14.753^{*}}{1 - 0.1840} \times \frac{100}{5} = 66.5\%.$$

If there were 30% kernels in the tung fruit, then the % oil in tung fruit = 66.5% × .30 = 19.95%.

COMPARISON OF RESULTS FOR OIL CONTENT OF OIL FRUIT

COMPARISON OF RESULTS FOR OIL CONTENT OF TUNG CONTENT by Solvent Extraction and Proposed Rapid Method

Sample No.	Per cent Oil by Solvent Extraction**	Per cent Oil by Rapid Method
1	17.47	17.43
2	17.07	17.23
3	17.15	17.15
4	20.81	20.75
5	18.21	18.27
6	18.29	18.36
7	20.05	20.21
8	17.71	17.80
9	20.50	20.90
10	12.32	12.21
Average	17.96	18.03

* This number represents the weight in grams of the acetylene tetrabromide delivered at 25° C. by the five-milliliter pipette used. If the particular pipette used delivers a different weight of this solvent at the temperature used, then this number should be replaced by the weight of solvent delivered by the pipette used.

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Cotton-Root Bark as a Source of Gossypol

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IN VIEW of the fact that the recent extensive researches of Adams and associates (1-20, 23, 24, 25) on the structure of gossypol have aroused wide interest in this compound, a brief description of a new and practical method for the preparation of pure gossypol is offered at this time. The proposed method is essentially a modification of that of Carruth (21), in which the precipitation of gossypol-acetic acid is applied to a solvent extract of cotton-root bark, rather than to an extract of the cotton seed. The advantages of cotton-root bark over the seed as a source of gossypol are chiefly the higher gossypol content and lower oil content of the root bark. The gossypol content of air-dried cotton-root bark has been found to range as high as 1.8 per cent, compared to about 1.0 per cent maximum for decorticated cottonseed meats, and the virtual absence of oil in the bark facilitates the separation and purification of the gossypol. Thus, the proposed method will yield about 0.9 per cent of purified gossypol, based on the air-dried bark, whereas, a good yield from seed is about 0.3 per cent (20).

Cotton-root bark, as a recognized drug (22), is obtainable from wholesale pharmacists, particularly in the South, although in this form its cost as a source of gossypol may be rather high. In the present investigation, it was found to be more economical to hire the labor to harvest, strip, and dry the cotton-root bark in the field, storing and grinding it in the laboratory as required. The most comprehensive available reference on the active medicinal principles in cotton-root bark, by Power and Browning (26), does not identify gossypol as one of the active ingredients, but a perusal of their experimental data leaves the impression that gossypol, or related phenolic substances, probably constitute a considerable part of the active material.

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DISTRIBUTION OF GOSSYPOL IN THE COTTON PLANT

As early as 1935 short staple cotton plants, gathered at various stages of maturity, were collected in this Laboratory, and the various parts of the plants were separated, air-dried, and analyzed for gossypol content by the pyridine-aniline method (27). All of the cotton plants analyzed in this work were upland short staple (1 inch), Delta and Pineland 11 A strain. The results in Table I are based on plants grown in 1936 near Meldrim, Georgia, on a sandy loam soil, in a season of average rainfall.

For the gossypol determinations, 10 grams of the dried, ground, plant structures were extracted exhaustively with cold ethyl ether, the extract evaporated at reduced pressure below 35° almost to dryness, and then taken up with 50 ml. petroleum ether (Skellysolve F). Any precipitate that formed was filtered off, washing the filter with petroleum ether, and 3 ml. of pyridine-aniline mixture (4:1) was added to the filtrate. The samples were then shaken, loosely stoppered, and allowed 3 to 7 days to precipitate, depending upon

TABLE I

Distribution of Gossypol in the Upland Variety Short Staple Cotton Plant at Various Stages of Maturity

Plant Structure	Percentage Gossypol, air-dry basis: A Immature Plant bolls just starting to form. July 15	B Mature green plant, most of bolls open. Sept. 15	C Dead Plant Jan. 15	D Dead Plant Feb. 15
Root Bark	0.70	1.53	1.80	1.82
Root (Whole)	0.25	—	—	—
Root (bark-free)	0.08	0.03	Trace	Trace
Stalk	0.05	0.0013	Trace	—
Leaf	Trace	Trace	—	—
Square	0.12	—	—	—
Boll	Trace (Immature boll)	0.18	—	—
Seed (Mature)	—	0.52	—	—