The Oil Content of Tung Products by a Rapid Petroleum Naphtha Method

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THE tung oil mills need a rapid, accurate procedure whereby samples of press cake and filter cake can be analyzed for oil content. Such a method can also be used at the mill for the analysis of small lots of tung fruit for oil content so that payment for the lot can be made without delay.

A number of rapid oil methods have been devised for determining the oil content of oleaginous seeds (2, 3, 4, 5), but none of the methods yields accurate results for oil contents of seeds high in moisture content. Another disadvantage of these methods is that they employ the use of either halogenated solvents, or petroleum solvents of high volatility. The use of halogenated solvents is objectionable because of their toxicity, unless adequate protection against their toxic vapors is available. The low boiling, highly volatile petroleum solvents are relatively nontoxic, but their use presents a fire and explosion hazard at the mill unless precautions are employed.

With a rapid petroleum naphtha procedure developed at this laboratory for the analysis of tung fruit, it has been found possible to obtain results for oil content of both air-dried and very wet samples of tung fruit which were in good agreement with results obtained with the Official Methods of the American Oil Chemists' Society. Equally good results were also obtained with samples of tung press cake and filter cake. In addition, the high boiling petroleum solvent (b.p. 312-387°F.) has a high flash point of 100°F. and so at ambient temperatures can be used safely at the mill, providing ordinary care is exercised.

The principles of this rapid petroleum naphtha method for determining the oil content of tung products are quite simple. A weighed portion of the finely ground sample is mixed for 10 minutes with twice its weight of a high boiling naphtha (sp. gr. 0.7817 @ 25°C.), the solution of oil in the solvent is filtered off, and its density is determined at 25°C. The oil content of the sample is then estimated from a specific gravity-percentage tung oil curve.

Preparation of Samples

The Official Methods of the American Oil Chemists' Society for determining the moisture and oil content of tung fruit (1) have been found to yield satisfactory results for the oil content of air-dried and very moist tung fruit. In these methods the sample of tung fruit is ground in a Wiley [2] mill through a ¼-in. screen, and the portion used in the oil determination is finely reground in a Bauer [2] No. 148 Laboratory Mill, using No. 6912 plates set 0.006 to 0.012 in. apart at 3,600 r.p.m. The same method of preparation is used in this rapid procedure for the analysis of tung fruit. As some drying occurs in the preparation of the Wiley-ground material for the oil determination, it is necessary to make a moisture determination on the Bauer-ground material, using the method employed on the Wiley ground material (1), and the oil content of the tung fruit is calculated to the original moisture basis.

Tung press cake samples are ground to a fine powder in a laboratory attrition mill before the application of this rapid petroleum naphtha method for determining their oil content. Filter cake samples require no grinding procedure but must be thoroughly mixed so that representative samples can be weighed for the oil analysis.

Preparation of Petroleum Naphtha Solvent

A petroleum solvent of constant specific gravity (0.7817 @ 25°C.) is prepared by mixing appropriate weights of two petroleum naphthas, Bronco [2] "Mineral Spirits L" with a specific gravity range of 0.7730-0.7817 @ 25°C., and Bronco [2] "No. 140 Solvent," with a specific gravity range of 0.7817-0.7906. The appropriate weights of any two lots of these solvents required to yield the petroleum naphtha solvent of specific gravity 0.7817 @ 25°C. are obtained from the following equation:

$$X(\text{sp. gr. "140"} - \text{sp. gr. "L"}) = 78.17 - 100 \times \text{sp. gr. "L"}$$

where X = Percentage by weight of "140"

$100 - X$ = Percentage by weight of "L"

Procedure

One hundred grams of petroleum naphtha (sp. gr. 0.7817 at 25°C.) are weighed into a 300-ml. beaker, and 50 g. of the finely ground sample are added. This mixture is thoroughly stirred at about 800 r.p.m. for 10 minutes, using a metal stirring rod with a 1½-in. diameter propeller attached to a stirring motor. The mixture is carefully filtered with suction through No. 2 filter paper in a Buchner funnel attached to a Witt filtering apparatus, and the filtrate is collected in a 150-ml. beaker. The specific gravity of the filtered solution is determined, using a pycnometer at 25°C. or a specific gravity balance, in which case the temperature of the solution is read in degrees centrigrade to the nearest tenth of a degree, and the specific gravity of the solution at 25°C. is calculated. For each degree the temperature of the solution is above 25°C., 0.0007 is added to the specific gravity at ambient temperature. If the temperature is below 25.0°C., the correction is subtracted. The oil content of the finely ground sample is obtained by reference to either specific gravity-percentage tung oil tables or curves prepared for tung fruit, press cake, and filter cake. In the case of the tung fruit samples the oil content of the fruit is calculated to the original moisture basis.

Preparation of Curves

a) *Tung Fruit.* A number of samples of tung fruit were analyzed for oil content, using the Official Meth-

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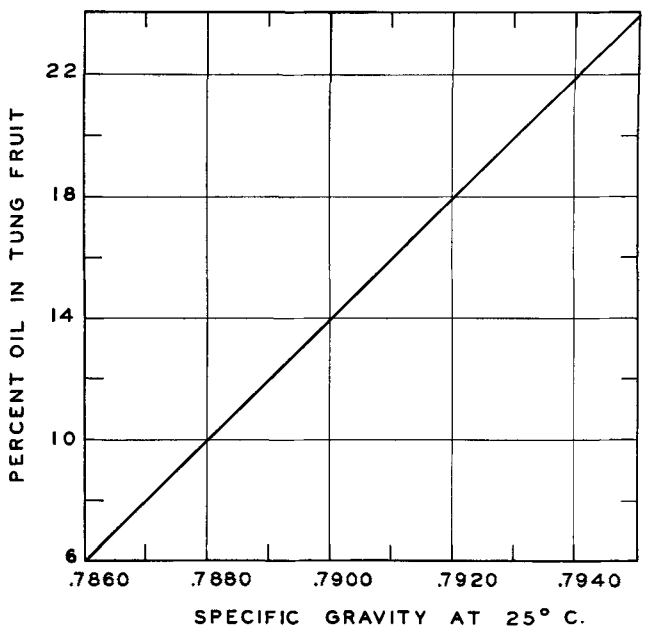
[2] Trade names have been used only for the purpose of identifying equipment or materials actually used in conducting the work, and such use does not imply endorsement or recommendation by the U. S. Department of Agriculture over other firms or similar products not mentioned.

ods of the American Oil Chemists' Society (1). Another portion of the samples of tung fruit, ground through the Wiley-Bauer[2] mills was used in the rapid petroleum naphtha procedure, and the specific gravity of the tung oil solution was determined at 25°C., using a pycnometer. From these data equation No. 1 was derived for the specific gravity of petroleum naphtha solutions at 25°C. for various percentages of oil in tung fruit. Equation No. 1: $SG^{25°C.} = 0.7818 + 0.00057 \times \%$ oil in tung fruit. A curve was drawn plotting percentage of oil in tung fruit against the specific gravity of the petroleum naphtha solutions at 25°C.

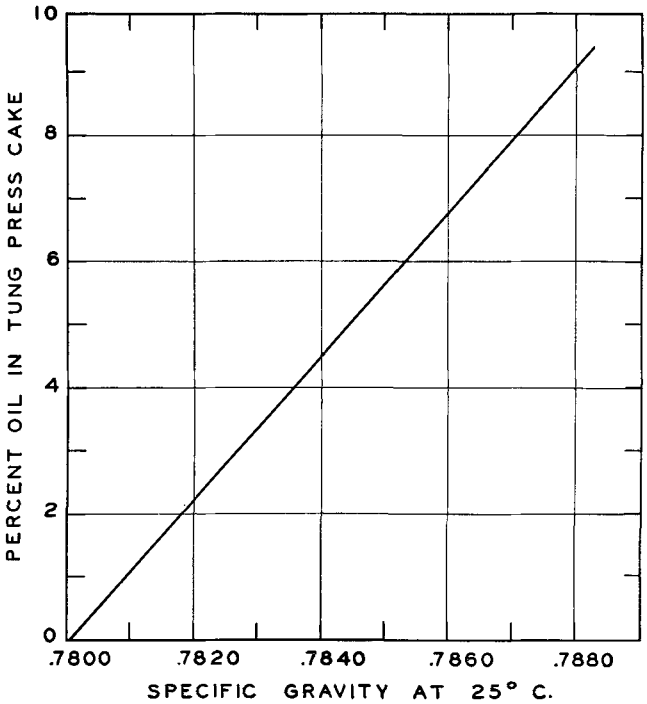


CURVE 1

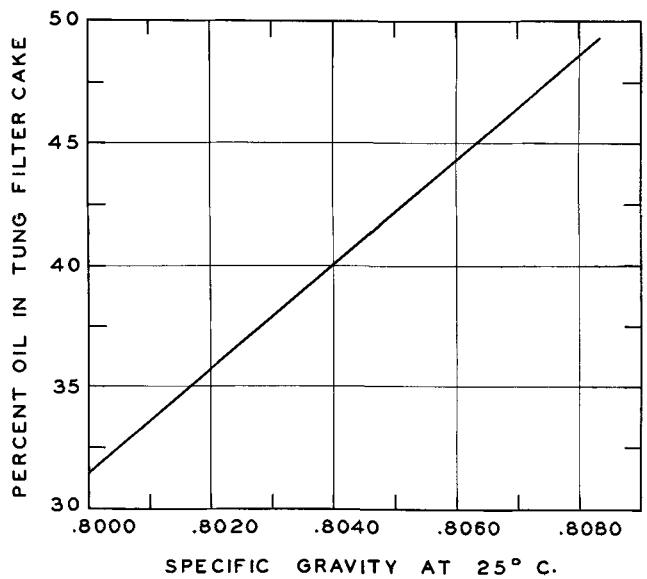
b) *Press Cake.* A number of samples of press cake were finely ground, and the samples were analyzed for oil content using a 4-hr. extraction period with petroleum ether. Another portion of each sample of ground press cake was used in the rapid petroleum naphtha procedure and the specific gravity of the tung oil solution was determined at 25°C., using a pycnometer. From these data equation No. 2 was derived for the specific gravity of petroleum naphtha solutions at 25°C. for various percentages of oil in tung press cake. Equation No. 2: $SG^{25°C.} = 0.7802 + 0.00085 \times \%$ oil in tung press cake.

c) *Filter Cake.* Samples of tung filter cake were analyzed for oil content, using a 4-hour extraction period with petroleum ether. Another portion of each sample of filter cake was used in the rapid petroleum naphtha procedure, and the specific gravity of the tung oil solutions was determined at 25°C., using a pycnometer. From these data equation No. 3 was derived for the specific gravity of petroleum naphtha solutions at 25°C. for various percentages of oil in tung filter cake.

Equation No. 3: $SG^{25°C.} = 0.7861 + 0.00045 \times \%$ oil in tung filter cake. A curve was then drawn plotting the percentage of oil in filter cake against the specific gravity of the petroleum naphtha solutions at 25°C.



CURVE 2



CURVE 3

Specific Gravity Balances

The Becker Specific Gravity[2] balance or the Westphal balance can be used as well as the pycnometer in this procedure, providing the specific gravity of the petroleum naphtha solvent is adjusted to a specific gravity of 0.7817 at 25°C. on the specific gravity balance or Westphal balance to be used in the oil determination. The value of results obtained with the specific gravity balances is based upon agreement with the measurements obtained with the pycnometer.

Results

The rapid petroleum naphtha method was applied to samples of tung fruit, press cake, and filter cake. Portions of these samples were also analyzed for oil

content, using the Official Methods of the American Oil Chemists' Society for Tung Fruit and Meal (1). The results obtained are given in Table I.

TABLE I
Analysis of Tung Fruit

Moisture	Oil			
	Extraction [a]	Pycnometer	Becker	Westphal
%	%	%	%	%
27.9	15.6	15.2	15.3	16.5
18.4	18.8	18.4	18.3	18.8
19.6	16.9	17.2	16.8	16.8
15.0	15.9	16.0	16.2	16.5
16.3	18.6	18.8	18.8	17.2
9.8	16.2	15.8	15.7	14.4
28.9	14.8	15.0	14.7	14.6

Analysis of Tung Press Cake

Moisture	Oil			
	Extraction [a]	Pycnometer	Becker	Westphal
%	%	%	%	%
4.2	9.0	9.2	9.2	8.5
5.7	5.0	5.2	5.3	5.3
4.9	6.9	6.7	6.8	7.3

Oil Content of Tung Filter Cake

	Extraction [a]	Pycnometer	Becker	Westphal
	%	%	%	%
	47.5	47.5	47.0	49.0
	46.7	46.5	46.1	46.5
	41.3	41.9	42.1	41.3
	41.5	41.0	41.2	40.8
	40.9	41.2	41.5	42.0
	42.6	41.9	41.2	42.6

[a] As described in AOCS Official Method Ad 3-52.

This new rapid petroleum naphtha method for determining the oil content of tung fruit, press cake, and filter cake gave results which were in good agreement with those obtained with the 4-hr. extraction with petroleum ether required in A.O.C.S. Official Method Ad 3-52. Better results were obtained with this method on high moisture content samples than with other rapid oil methods probably because the method of preparation disintegrated the oil cells of tung kernels to an extent not possible in other methods of preparation even in the presence of relatively large amounts of water. With the pycnometer the standard deviation of the results for oil content of samples of tung fruit, press cake, and filter cake were 0.3, 0.4, and 0.5% oil, respectively; with the Becker balance the standard deviations were 0.3, 0.4, and 0.9% oil, respectively, while with the Westphal balance they were 0.9, 0.5, and 0.9% oil, respectively.

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A Laboratory Distillation Method for the Evaluation of Crude Glycerin

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THE conventional analysis of crude glycerin generally includes the net glycerol, ash, organic residue, free alkalinity, and the Na_2O equivalent of organic matter. While the foregoing analysis indicates whether the crude has been properly processed, it gives us no definite indication of refining yield to be expected.

The purpose of this work was to establish a laboratory distillation method for evaluating crude glycerin to supplement the analytical information. The pertinent questions to be answered by such a project were:

a) What yields can be obtained from various grades of crudes in a controlled laboratory distillation?

b) What is the accuracy of the method?

c) What property or properties of crudes most markedly influence the laboratory distillation yields?

With the proper resolution of these questions one could expect to be better equipped to predict plant refining yields.

Experimental Work

A simple vacuum distillation apparatus was used. The apparatus, illustrated in Figure 1, consisted of a 200-ml. round-bottom, long-neck flask, connected to a short side arm distilling head. A short water-cooled

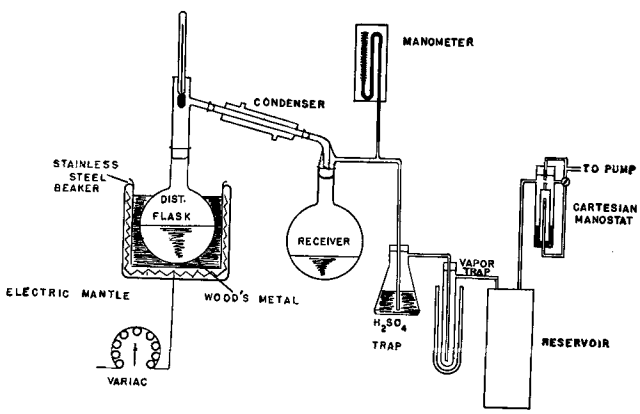

FIG. 1. Laboratory distillation apparatus.

condenser was used to condense the glycerol vapors. The distillate was collected in a receiver similar to the distilling flask. The heating bath consisted of Woods metal (m.p. 72°C.) in a 1-liter, stainless steel beaker enclosed in a heating mantle. A McLeod and a differential manometer were used to indicate the pressure, the former to give precise spot readings and the latter to give continuous indication of the pressure. The water vapors were removed before reaching the pump by means of a sulfuric acid trap and a cold trap connected in series. A 10-gal reservoir was