Some Notes on the Determination Of Moisture And Volatile Matter in Fats And Oils

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It has been recognized for some time, that the common methods for the determination of moisture and volatile matter in fats and oils are not applicable to all fats and oils, nor are any, with the possible exception of the vacuum oven method, suitable for the accurate determination of the very small percentages of moisture normally present in clean refined oils. The limitations of some of these methods are chemical, while in others the limitations are in the manipulation of the method or in the technique required.

In February 1926, the methods which were adopted in 1919 by the Fat Analysis Committee of the American Chemical Society, were revised and adopted by the Fat Analysis Committee of the American Oil Chemists Society, acting also as the American Chemical Society Committee on Analysis of Commercial Fats and Oils. These methods were:

1. The Vacuum Oven Method
2. The Air Oven Method
3. The Hot-Plate Method
4. The Kingman Distillation Method

The procedure outlined for these methods are well known and do not require further elaboration here.

Jamieson in 1931, observed that when the moisture of drying or semi-drying oil is determined in the air oven, an atmosphere of inert gas, such as CO₂ should be maintained in the oven; and that the hot-plate method gave the highest results, while the closest checks were obtained in the vacuum oven.

He reported that on crude Menhaden oil, the hot-plate method gave moisture results varying between .09 and .19%, the air oven method between .02 and .08%, and the vacuum method from .04 to .08%.

In the official and tentative methods of the American Oil Chemists revised in 1938, the following information concerning moisture and volatile matter was given: “With all methods for determining moisture by means of loss on heating, there may be a loss due to volatile matter other than water. The title of the determination ‘Moisture and Volatile’ indicates this, but any considerable error from this source may occur only in high acid fats and oils, and particularly those containing lower fatty acids such as coconut and palm kernel oil....”. “The Committee found by individual, cooperative, and collaborative work by several of its members in one laboratory, that the old well-known direct-heating method which the Committee has designated the Hot-Plate Method, yields very satisfactory results on all sorts of fats and oils....”

Of the four methods, the Kingman Distillation Method is the only one that permits the determination of actual moisture present in an oil or fat. While valuable for moisture determinations on fats and oils containing appreciable percentages of water, it is obviously not suited for fats and oils having moisture contents much below 0.5%.

Although the hot-plate method may be suitable for routine control tests, and there may be some question of this from an accounting standpoint, it has definite limitations and has not proved satisfactory on low moisture oils, particularly on prime summer yellow cotton oil of which the N.C.P.A. rules state that the dissolved moisture content must not be in excess of .05%. A serious limitation to this method lies in the lack of a temperature control, which was emphasized by Freyer’s report that Hot-Plate Method of bringing a sample to incipient smoking caused high results in soybean oil. He suggested that the method be changed to provide a definite maximum temperature to which the oil should be heated and that should this be done, some hot-plate of controlled and indicated temperature as described in his report would be required.

We have found that if heating is carried momentarily to incipient smoking, as specified in the method, the temperature of a sample of soybean oil reaches about 235°C. If a strong beam of light is used to observe the first traces of smoke, the temperature of the sample reaches approximately 215°C. Even this difference in temperature materially affected the moisture results and quite concordant values were obtained when the strong beam of light was used. Dean gives a method for determining moisture and volatile matter in fats and oils, in which a flat-bottomed sample dish containing a small thermometer is placed on a sand-bath heated with a low flame while stirring constantly and without exceeding a temperature of 105°C.

On semi-drying oils of low moisture content, the air oven method is far from accurate, and is not recommended in the moisture methods for oils in the drying or semi-drying classes. In a number of cases where an attempt was made to determine the moisture of refined cottonseed oil in the air oven, we have had an actual gain in weight of the sample; whereas, duplicate samples tested by the Hot-Plate Method, showed moisture contents varying from .06 to .09%. If, however, peroxide numbers of samples from the air oven are determined and the calculated weight of active oxygen absorbed by the oil is subtracted from the weight of the dried sample, much more accurate results are obtained.

The vacuum oven method has given quite reliable moisture results on the drying and semi-drying oils, but cannot be considered accurate for high-fatty-acid oils of the coconut group.

A paper, presented at the spring meeting of the Oil Chemists Society at Dallas in 1937, by Parsons
and Holmberg, on the "Estimation of Water in Salad Oil and Determination of its Solubility at Ordinary Temperatures," pointed out that a distinct need existed for a method which would permit the determination of small amounts of water in the oils, preferably by weighing the water evolved after absorption in some suitable medium. A simple apparatus was described, in which 10 to 50 gram samples of the weighed oil were dried in a current of inert gas at 130-140° C., the moisture being absorbed in fused calcium chloride. This same procedure has been used effectively by our laboratories as a check on the other methods of moisture determination. We have found that the absorption method is absolute and is especially suited for moisture determinations of all types of oils having relatively low moisture contents, except those containing a residual solvent.

The absorption method is simple, inexpensive, and does not require a highly developed technique. The presence of an inert gas prevents oxidation, and the size of the sample used minimizes errors of manipulation and weighing. This method, however, has the disadvantage of limiting the number of tests that can be determined at one time.

Parsons and Holmberg used H₂ as the inert gas and 10 to 50 grams of oil, depending on the moisture content of the sample. We have used nitrogen and a sample weight of 100 grams. Figure I presents a sketch of the apparatus. In practice, a T-tube is inserted at point A, thus allowing two sample lines to be in operation at the same time. The nitrogen is purified by washing with Burrell's Cosorbent and sulphuric acid, and is further dried by passing through a U-tube containing anhydrous CaCl₂.

When determining moisture of refined oils, the nitrogen is bubbled at a rate of about 80 - 90 cc. per minute directly through the sample heated to 150° C.; but with some crude oils, it is necessary that the entry tube be above the surface of the sample, or excessive foaming will be encountered. The two methods of introducing the gas, however, give identical results on refined oils. The moisture carried out by the nitrogen is absorbed in two Schwartz tubes filled with anhydrous CaCl₂.

A series of trial runs indicated that about two hours were required to completely remove the moisture from a 100 gram sample. All connections must be gas-tight, and it is advisable to use exceptionally heavy stop-cock grease on all ground-glass joints.

In order to determine if the absorption method was absolute, known percentages of water were added to several samples of PSY cottonseed oil and the amount of recoverable moisture determined. The results of these runs are presented in Table I.

An average recovery of 96.9% was obtained with an average deviation of only .7%. This means a difference of only slightly more than .01% between determined and calculated values on a sample containing as high as .3% moisture.

In comparison of the methods recommended for moisture and volatile matter, cottonseed, soya-bean and coconut oils were selected as these oils cover a rather wide range of moisture requirements. The absorption method was taken as standard. The average data obtained on cotton, soya and coconut oils in this comparison are presented in Table II.

It is indicated from these results that the vacuum oven gives the most concordant results of the recommended methods, although it still does not approach the agreement obtained by the absorption method.

Table III shows the change in moisture results due to increase in peroxide number during the moisture determination of the same samples presented in Table II.

The increase in peroxide number is negligible and therefore has no effect on the moisture results of the nearly saturated coconut oil, and but little on crude cottonseed and soya oil samples which contain natural anti-oxidants. The increase in peroxide number of samples of refined cottonseed oil and soya oils during the moisture determination in the air oven exerts a marked influence on the moisture results. Peroxide increase on moisture samples of these two oils run in the vacuum oven affect moisture results slightly. The negligible peroxide number increase in moisture samples of refined cottonseed oil and soya oils when run on the Hot...