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[1], 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[2] 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 CO_2 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[3] 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[4] 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[5], 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 oils 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[6], 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 dryed 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 H_2 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 allowng 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 $CaCl_2$.

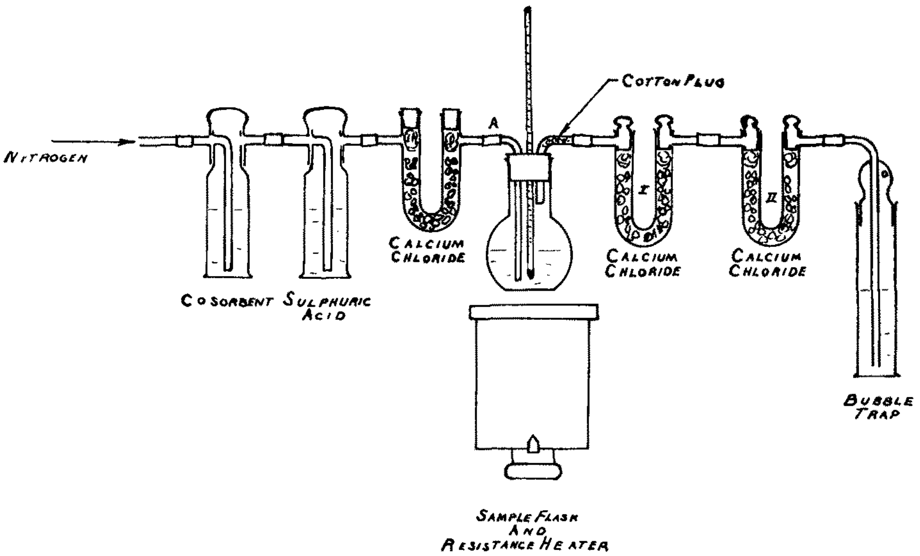

FIGURE I. ABSORPTION APPARATUS

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 $CaCl_2$.

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, soyabean 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 soyabean oils 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-

TABLE I

ABSORPTION METHOD — % ADDED WATER RECOVERED

SAMPLES — 100 GRAMS PSY COTTON OIL — ORIGINAL MOISTURE .0741%

Run No.	Grams H_2O Added	Grams H_2O Recovered Tube I	Grams H_2O Recovered Tube II	% H_2O Determined	% H_2O Calculated	% Total H_2O Recovered
1	.0000	.0750	.0016	.0766	—	—
2	.0000	.0714	.0011	.0725	—	—
3	.0000	.0617	.0116	.0733	—	—
4	.1198	.1856	.0000	.1856	.1939	95.7
5	.1265	.1942	.0004	.1946	.2006	97.0
6	.1600	.2251	.0015	.2266	.2341	96.8
7	.1662	.2314	.0010	.2324	.2403	96.7
8	.1953	.2549	.0119	.2668	.2694	99.0
9	.2441	.3027	.0036	.3063	.3182	96.2
					Average	96.9
					Average Deviation	.7

TABLE II
COMPARISON OF MOISTURE RESULTS ON COTTON, SOYA, & COCONUT OILS DETERMINED BY VARIOUS METHODS (WITHOUT PEROXIDE CORRECTION)

	Absorption			Hot Plate				Air Oven				Vacuum Oven			
	No. Tests	% H_2O	% Dev.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.
Crude Cottonseed	4	.151	.7	5	.160	12.5	+6.0	5	.125	26.4	—17.2	5	.097	4.1	—35.7
Refined Cottonseed	6	.070	1.4	5	.125	9.6	+78.6	7	.043	32.6	—38.6	8	.064	21.9	—8.6
Crude Coconut	4	.158	.6	5	.160	12.5	+1.3	5	.458	12.9	+189.9	7	.208	7.2	+31.6
Refined Coconut	4	1.47	.1	5	1.48	10.8	+.7	5	1.48	3.4	+.7	4	1.46	1.4	—.7
Crude Soya (Exp.)	4	.074	2.2	5	.137	14.6	+85.1	5	.011	26.3	—85.1	10	.038	18.4	—35.1

TABLE III
COMPARISON OF MOISTURE RESULTS ON COTTON, SOYA, & COCONUT OILS DETERMINED BY VARIOUS METHODS

(TABLE II CORRECTED FOR CHANGE IN PEROXIDE NUMBER)

	Absorption			Hot Plate				Air Oven				Vacuum Oven			
	No. Tests	% H_2O	% Dev.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.	No. Tests	% H_2O + Vol.	% Dev.	% Dev. From Absorp.
Crude Cottonseed	4	.151	.7	5	.160	12.5	+6.0	5	.148	26.4	—2.0	5	.099	4.1	—34.6
Refined Cottonseed	6	.070	1.4	5	.125	9.6	+78.6	7	.086	32.6	+22.8	8	.075	21.9	+7.0
Crude Coconut	4	.158	.6	5	.160	12.5	+1.3	5	.458	12.9	+189.9	7	.208	7.2	+31.6
Refined Coconut	4	1.47	.1	5	1.48	10.8	+.7	5	1.480	3.4	+.7	4	1.46	1.4	—.7
Crude Soya (Exp.)	4	.074	2.2	5	.137	14.6	+85.1	5	.021	26.3	—58.0	10	.038	18.4	—35.1

Plate may be attributed to a peroxide destruction at the temperature at which the test is conducted. The high moisture results obtained on these two oils by the hot-plate method, indicate that there is a loss in weight of the samples due to volatilization of some fatty portion not normally driven off in tests conducted at lower temperatures.

In order to further compare the accuracy of the method, a series of seven samples of PSY cotton oil of known moisture content ranging from .1 to .9% were made up and duplicate samples run by each method. The results are shown in Table IV.

TABLE IV
Percent Recovery of Added H_2O by Various Methods

	Without PN Correction		With PN Correction	
	Average % Recovery	Mean Dev. as % H_2O	Average % Recovery	Mean Dev. as % H_2O
Vacuum Oven	85.0	.005	89.2	.005
Air Oven	40.1	.006	89.3	.033
Hot Plate	115.7	.022	115.8	.022
Modified Hot Plate	88.3	.007	88.3	.007
Absorption	96.9	—	96.9	—

Here the superiority of the vacuum oven is shown even more clearly than in Table II. Although the air oven gives practically the same percentage recovery as the vacuum oven after correcting for absorbed oxygen, the variation between duplicate samples was considerably greater. Hot-plate moistures were run on the same series of samples using a strong beam of light, as previously described, in order to detect the first traces of smoking. This modified procedure gave very good results with an average recovery of 88.3% uncorrected for peroxide number, and an average deviation between samples of only .007% in actual moisture content. The method thus gives moisture results approaching those of the vacuum oven which have been corrected for oxygen absorption.

In determining moistures of samples of crude extracted soyabean oil by the vacuum-oven and hot-plate methods, a number were found to contain relatively high per centages of moisture and volatile matter. Kingman-Distillation tests on 500-gram samples of these same oils indicated that the percent of actual water present was indeed slight, as the volume of water distilling over was so small that accurate estimation was impossible. The differences existing in percent moisture and volatile matter between these methods on duplicate samples were attributed to residual solvent in the oils.

By simply adding an absorption tube filled with activated carbon to the train used in the absorption method, a test was devised that not only determines the water present in an oil, independent of any volatile matter, but also determines by direct absorption at the same time, the percent of residual solvent in an extracted oil. A 14-35 mesh carbon of coconut origin, activated for gas adsorption, was used.

We have found this method for residual solvent to be absolute, and recovery of 100% of added solvent is possible if certain conditions and precautions are observed. In order to obtain reliable results and insure 100% adsorption, it is necessary to out-gas the activated charcoal in the Schwartz tube at about 500°C. for 5 to 10 minutes, under as high a vacuum as is possible (at least 29.5+ inches is desirable). In outgassing the charcoal, the filled tube was placed in an air bath directly over a 250-watt unit heater.

A suitable air bath may be improvised from an open 1-lb. tin shortening container by cutting a slot approximately 2 inches by ½ inch in the bottom, through which the U-tube is inserted. When the vacuum is broken, connection is immediately made with a cylinder of nitrogen, and the gas passed through the tube during and after cooling until two consecutive weighings are within two milligrams.

It is also important that the flow of gas through the tube during a run be approximately 70-90 cc. per minute, as a higher velocity tends to sweep the solvent vapors and also adsorbed solvent from the tube. Temperature control must be fairly close, as higher temperatures seem to give much higher results, probably due to the adsorption of vapors of the lower fatty acids present in the oil being tested. At a temperature of 150°C., however, there was little or no gain, and in some instances even a slight loss in weight in the carbon tube when running expeller or hydraulic oils. Although there were no indications of saturation of the 8

TABLE V
RECOVERY OF ADDED SOLVENT BY THE ADSORPTION METHOD

Run No.	Solvent Added	Grams H_2O Retained in $CaCl_2$ Tube I	Grams H_2O Retained in $CaCl_2$ Tube II	Grams Solvent Recovered in Carbon Tube	% H_2O Determined	% Solvent Determined	% Recovery of Solvent
1	.0967	.0450	.0090	.1015	.0540	.1015	105.0
2	.1005	.0508	.0012	.1069	.0520	.1069	106.4
3	.2066	.0519	.0052	.2099	.0571	.2099	101.6
4	.2104	.0527	.0027	.2083	.0554	.2083	99.0
5	.3153	.0461	.0046	.3126	.0507	.3126	99.1
		Average			.0538		102.2
		Average Deviation			.0020		2.8

TABLE VI
COMPARISON OF METHODS ON EXTRACTED AND EXPELLER SOYA BEAN OILS

	% H_2O & Volatile			Absorption Method		
Oil	Hot-Plate	Air Oven	Vacuum Oven	% H_2O Determined	% Solvent Determined	% H_2O & Solvent Determined
Extracted No. 1 Av.	.342	.226	.352	.077	.274	.351
Extracted No. 2 Av.	.236	.142	.119	.143	.027	.170
Extracted No. 3 Av.	.209	.074	.105	.125	.047	.172
% Average Deviation from Absorption Method	16.1	36.2	16.8	—	—	—
Expeller No. 1 Av.	.137	.011	.079	.074	.000	.074

to 10 grams of charcoal in the tube after approximately 40 runs, it would probably be best to out-gas it after 30 - 50 runs to reduce the possibility of evaporation losses from the more nearly saturated charcoal.

To test the absoluteness of the method, known percentages of Skellysolve B were added to samples of refined cottonseed oil, and the amount of moisture and percent of solvent determined on each sample. The results of these runs are presented in Table V.

The recovery of solvent averaged 102.2% with an average deviation in percentage of only 2.8 over the entire range. It can be seen from the table that the percent of moisture determined in the various samples was entirely unaffected by the percent of solvent present.

Table VI gives the results obtained by this method on a number of samples of extracted soyabean oil and one expeller oil as compared with the figures obtained by the air oven, vacuum oven, and hot-plate on this type of oil.

The results of the vacuum oven are below the actual values of the sums of moisture and solvent, while the hot-plate results are somewhat high.

SUMMARY

It has been found that the method of moisture determination introduced by Parsons and Holmberg, in which water is evolved from the sample and absorbed on $CaCl_2$, is absolute and is applicable to all types of oils and fats, except those containing residual solvent. It is particularly suited for the determination of very low percentages of moisture in oils and fats.

Of the methods recommended by the A.O.C.S. for the determination of moisture and volatile in oils and fats, the vacuum oven was found to be the most accurate, except on high-fatty-acid coconut oil.

The hot-plate method gave the highest moisture results when the test was conducted according to the procedure outlined in the methods of the A.O.C.S. When first traces of smoking were observed under a strong beam of concentrated light, resulting moistures approached those obtained by the vacuum oven.

Moisture results obtained by the air oven, if corrected for peroxide absorption, approach those of the vacuum oven.

The percent of residual solvent in extracted soyabean oil, independent of moisture, may be accurately determined by adsorption of solvent vapor on activated charcoal.

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A Rapid Method For The Determination of Iodine Number

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THE standard method for the determination of Iodine Number as adopted by the Fat Analysis Committee of the American Oil Chemists Society and the American Chemical Society (1) requires thirty minutes absorption time for most fats and oils and stipulates one hour for tung, linseed and perilla oil. In general it has been found that any oil or fatty acid with an Iodine Number in excess of one hundred and thirty-five should be allowed one hour absorption time. Thus, the overall time required for an Iodine Number determination runs from about forty-five minutes to one hour and fifteen minutes depending on the absorption time required. In consequence, this method does not meet the requirements for rapid control of continuous plant operation. The present paper proposes a slight modification, of the standard method, which reduces the absorption time to three minutes.

Considerable work has been published by various investigators on the halogen absorption of fats and oils. However, the exact nature of the reaction has not been definitely established, the various theories advanced being somewhat conflicting.

Hubl (2) has suggested the use of mercuric chloride in conjunction with an iodine-alcohol solution. However, several hours are required for complete absorption by this method.

Wijs (3) has attempted to show that by increasing the concentration of hypoiodous acid in the Hubl solution through the addition of