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 iodine, mercuric chloride and water, more rapid absorption takes place. He also states that when a solution of hypoiodous acid is mixed with an oil, values identical with the Hubl Iodine Numbers are obtained, the absorption being complete in ten seconds. However, he cites only one example and does not show further investigation of the use of this solution, probably because of the great difficulty in the preparation and preservation of the hypoiodous acid. Later Wijs proposed to substitute for Hubl's solution a solution of iodine monochloride in glacial acetic acid. This Wijs solution, as adopted by the Committee, greatly reduced the absorption time as required by the Hubl solution.

More recently Scotti (4) proposed a method in which mercuric acetate is used as an accelerator in in conjunction with a solution of iodine, *in* pure benzol. The mercuric acetate is dissolved in glacial acetic acid and added to the fat directly after the addition of the iodine-benzol solution. He reports that absorption is practically instantaneous and cites data indicating that two minutes is sufficient.

A brief investigation of this method verified his data showing a very rapid halogen absorption. However, it did not appear that the iodine-benzol solution would be as satisfactory as the Wijs solution. Therefore, the use of mercury salts in conjunction with the Wijs solution was investigated. Preliminary tests showed that both mercuric acetate and mercuric chloride dissolved in glacial acetic acid, reduce the absorption time substantially. The mercuric acetate is more soluble in glacial acetic acid and reduces the absorption time more than the mercuric chloride. Further investigation was therefore confined to the use of mercuric acetate.

Experiments were conducted to determine the relative absorption rate with various amounts of mercuric acetate. The procedure followed in making these tests was the same as that prescribed by the official method except that various amounts of mercuric acetate dissolved in glacial acetic acid were added directly after the addition of the Wijs solution and the absorption determined at different contact intervals. For uniformity and accuracy of sampling a volumetric solution of the oil in carbon tetrachloride was prepared and equal parts taken for the individual determinations. These tests were made at a temperature of 27 ± 1° C. and all reagents had previously been allowed to reach equilibrium at this temperature. The excess of iodine was kept constant at about sixty percent. The results of these tests are shown in Figure I.

These results indicate that with two hundred and fifty milligrams of mercuric acetate complete absorption is obtained in one minute and that no further absorption occurs even up to one hour.

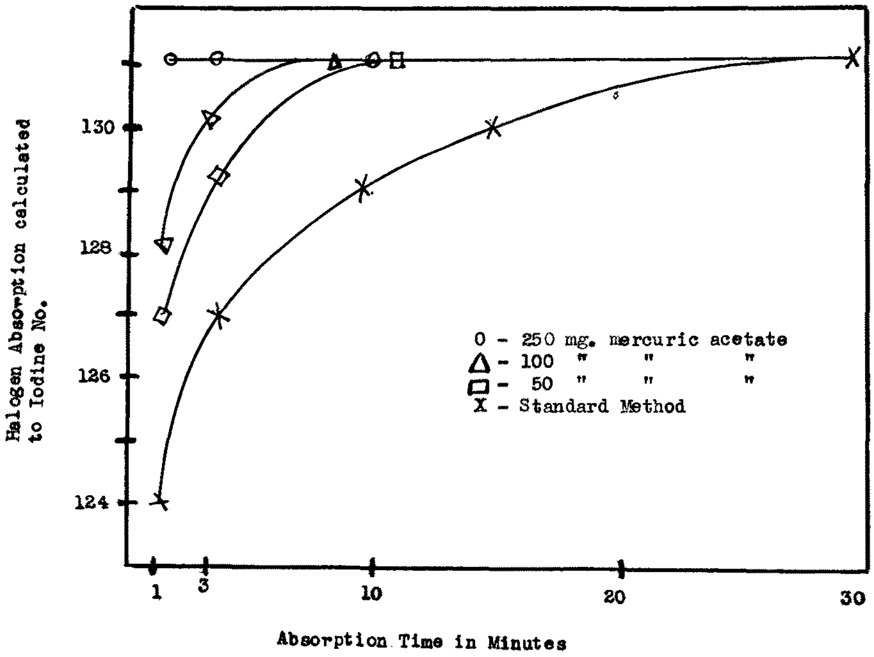

FIGURE I
Showing rate of halogen absorption by soya bean oil from Wijs solution with various amounts of mercuric acetate

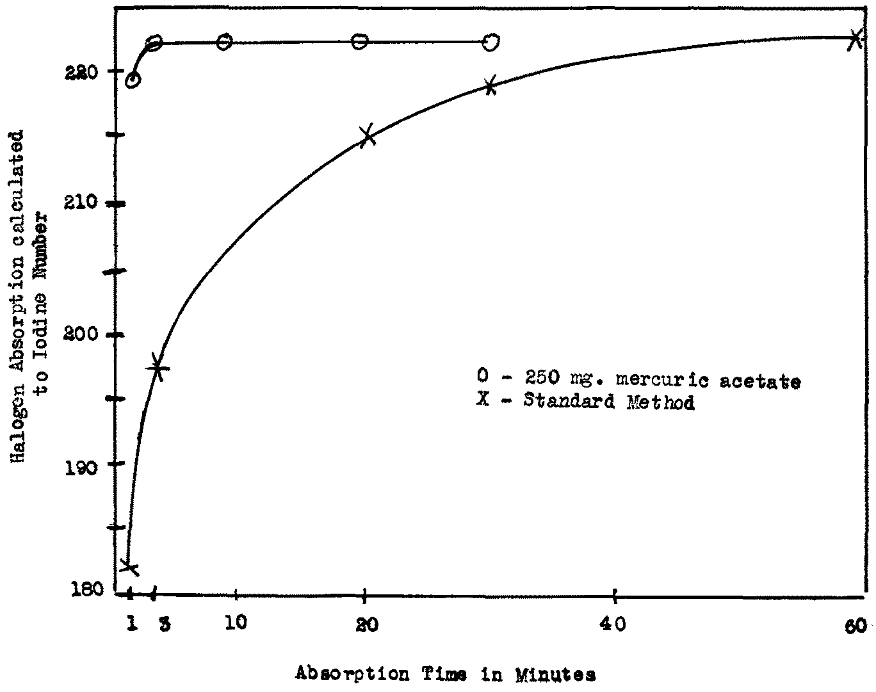

FIGURE II
Showing rate of halogen absorption by a highly unsaturated fatty acid from Wijs solution with and without mercuric acetate.

Similar tests were made on more highly unsaturated oils and fatty acids to show the comparative absorption rates by the standard method and with two hundred and fifty milligrams of mercuric acetate. Figure II shows these results on a highly unsaturated fatty acid, Figure III on linseed oil and Figure IV on cottonseed fatty acid.

These results show that even with highly unsaturated fatty acids and oils complete absorption is reached in three minutes using two hundred and fifty milligrams of mercuric acetate.

Further comparative tests were made at various temperatures with results as shown in Table I.

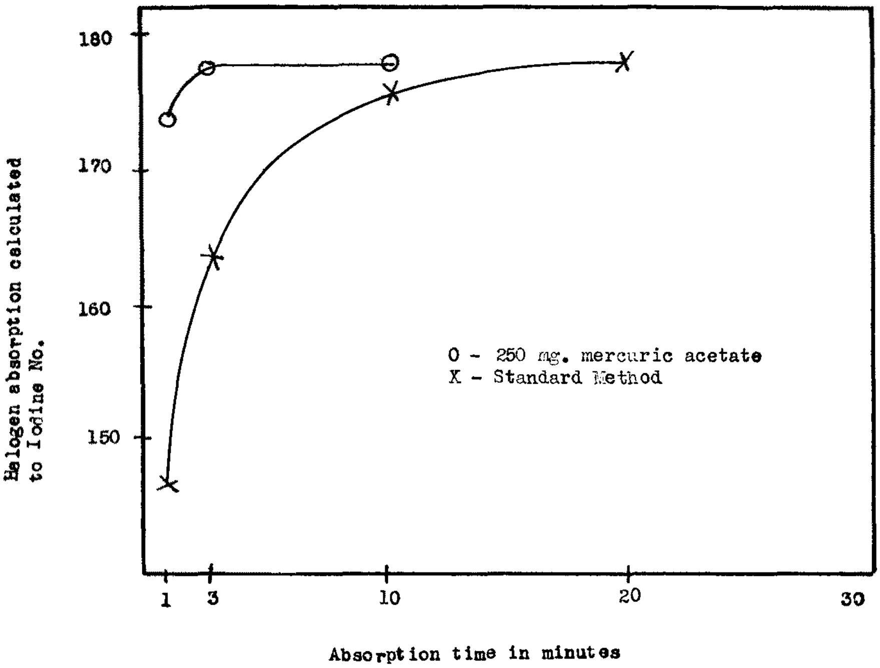

FIGURE III
Showing rate of halogen absorption by linseed oil from Wijs solution with and without mercuric acetate.

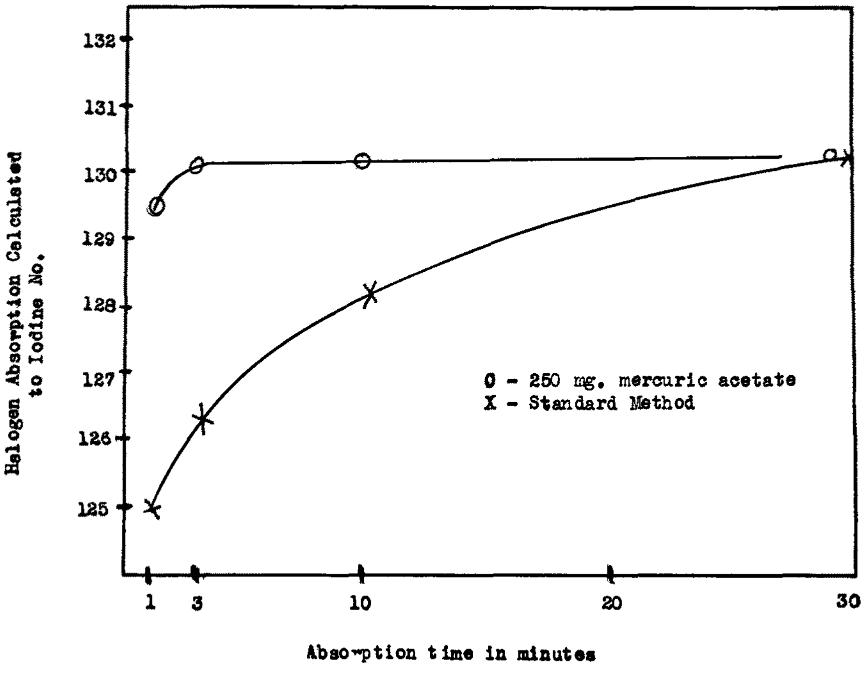

FIGURE IV
Showing rate of halogen absorption by cottonseed fatty acid from Wijs solution with and without mercuric acetate.

TABLE I

	21° C.	27° C.	35° C.
STANDARD METHOD			
Linseed Oil	175.0	175.6	176.5
Unsaturated Fatty Acid	224.0	224.0	227.0
MODIFIED METHOD			
Linseed Oil	175.5	175.5	176.1
Unsaturated Fatty Acid	223.8	223.4	225.0

These tests indicate that even at 21° C. complete absorption is obtained in three minutes by the modified method. At 35° C. both methods show high results.

As a further confirmation, a variety of oils were tested by the modified method and by the standard method. The details of the modified method were the same as the standard method except that ten milliliters of a two and one-half percent solution of mercuric acetate in glacial acetic acid was added directly after the addition of the Wijs solution and an absorption time of only three minutes allowed. The results of these tests are shown in Table II.

TABLE II

	IODINE NUMBER	
	Standard Method	Modified Method — 3 min.
Hydrogenated Sardine Oil	18.4	18.2
Palm Oil	48.8	49.0
Olive Oil	83.1	83.2
Soya Bean Oil	133.5	133.5
Cottonseed Fatty Acid	95.5	95.3
Special Fatty Acid	136.8 1 hr.	136.4
Sardine Oil	177.5 1 hr.	178.0
Linseed Oil	175.9 1 hr.	175.5
Unsaturated Fatty Acid	214.2 1 hr.	214.5
Chinawood Tung Oil	164.0 1 hr.	181.0
Oiticica Oil	145.0 1 hr.	138.0

It will be noted that the standard and modified methods do not give equivalent values on tung oil and oiticica oils. However, these are abnormal oils and it is known that the iodine absorption is erratic and does not represent the true unsaturation due to the presence of conjugated double-valence bonds.

In conclusion, it is suggested that accurate Iodine Numbers may be determined rapidly by modifying the standard method in the following manner. Add 10 cc. of a 2½% solution of mercuric acetate dissolved in glacial acetic acid to the sample directly after adding the Wijs solution. Allow three minutes absorption time and proceed with the determination as in the standard method. Several months of use has confirmed the value of this modification.

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