REPORT OF THE COMMITTEE ON SOAP IN REFINED OIL

DURING the past year the Committee has undertaken to test 4 published methods for the determination of soap in refined oil and one previously unpublished method. These methods were, two proposed by R. Durst (1) and referred to herein as the Durst Method and the Durst Ashing Method, two published by the Soap in Refined Oil Committee of 1935 to 1937, and referred to herein as the Alcohol Extraction Method (2) and the Free Fat Acid Method (3) and a modified Durst Method proposed by R. C. Stillman of the present committee. The procedures used in each of these methods follow:

DURST METHOD (1)

Weigh 300 grams of oil into a liter separatory funnel. Wash four times with 50 ml. portions of hot 1:1 hydrchloric acid. Combine the washings in a clean 250 ml. beaker and evaporate to dryness, heating carefully to prevent spattering. Take up the residue in distilled water and evaporate again to dryness. Repeat the last step twice more. Take up the final residue in 50 ml. of distilled water and heat nearly to boiling, add 1 ml. of 10 per cent potassium chromate solution and titrate with standardized silver nitrate solution to the usual end point. A convenient silver nitrate solution is one in which 1 ml. is equivalent to .01 gram of salt. The final calculation is made on the basis that one mol of sodium chloride is equivalent to one mol of sodium oleate. It is necessary to run a blank on the reagents.

DURST ASHING METHOD (1)

Carefully ignite a weighed amount of oil in a clean platinum crucible or evaporating dish. After the ignition is complete, place the crucible in a clean beaker and extract the ash with 1:3 hydrochloric acid. Carefully wash the crucible with a stream of distilled water, catching the wash water in the beaker with the acid. Evaporate the combined washings to dryness, take up the residue in distilled water and repeat the evaporations as in the first Durst method. The procedure from this point is identical to that in the first Durst method. It is necessary to run a blank on the reagents.

MODIFIED DURST METHOD (R. C. Stillman)

Weigh 125 grams of oil into a 500 ml. extraction cylinder and thoroughly agitate with 25 ml. of concentrated HCl. One hundred ml. of hot water (70°) is pipetted into the oil and acid and after vigorous agitation, the acid and water are allowed to separate and cool. Pipette 100 ml. of the water-acid solution into a beaker or large test tube, evaporate to dryness, add water and evaporate to dryness. Repeat. Take up the residue with 10 ml. hot water, cool to room temperature or below, add 2 ml. of potassium chromate solution and titrate with N/100 Ag NO_3. A blank on the water and HCl is run.

ALCOHOL EXTRACTION METHOD (2)

Weigh 100 grams of oil in a 200 ml. extraction cylinder. Extract with 50 ml. of hot alcohol (formula 30) by shaking vigorously, allow to settle and siphon off the alcohol into a 500 ml. beaker. If an emulsion is encountered, place the cylinder in hot water to facilitate the separation of alcohol and oil. Repeat the extraction procedure until a total of *five* washes have been made.

Evaporate the alcohol from the combined washes to a volume of 20-30 ml. and transfer to a platinum crucible, carefully washing the beaker with alcohol and transferring the washings into the crucible. Slowly burn off the alcohol and then ignite the crucible until no carbon remains.

Cool the crucible and place it into a 250 ml. beaker. Wash the crucible with about 50 ml. of hot distilled neutral water and titrate with N/50 HCl using methyl orange as an indicator. Run a blank on all the reagents.

1 c c. N/50 HCl = .00607% sodium oleate.

FREE FAT ACID METHOD (3)

Weigh 50.0 Grams of the oil into a 250 ml. separatory funnel. Add 50 ml. of distilled water heated to about 150° F. and shake for two minutes. Add 5 ml. N/2 HCl and shake vigorously for 5 minutes. Allow to settle and draw off the water. Wash the oil remaining in the separatory funnel with 50 ml. portions of hot water until the wash water is neutral. Three or four washes are usually sufficient. Draw off the washed oil into a 250 ml. beaker and place in a hot water bath at about 70° C. for 10 minutes to settle the water. Filter the oil to remove any remaining moisture and determine the F. F. A. as oleic using N/50 NaOH. The F. F. A. of the original oil must be determined at the same time using the same reagents and stopping at exactly the same end point. If a 28.2 gr. sample is used, per cent F. F. A. as oleic = ml N/50 NaOH × .02, and F. F. A. treated oil — F. F. A. original oil × 1.08 = % of soap as sodium oleate.

Two series of samples comprising two samples each were distributed to the members of the committee. These samples were cottonseed oils treated as follows:

1st Series No. 1—Refined, settled, water-washed;
1st Series No. 2—Refined and settled but not washed.
2nd Series No. 1—Refined oil high in soap;
2nd Series No. 2—Same oil as No. 1 but with 100 ppm. anhydrous, neutral, cottonseed oil soap added.

Sample No. 2 of the second series was prepared by dissolving the required amount of anhydrous soap in warm Formula 30 alcohol and mixing this alcoholic solution into a portion of the same oil that was used for sample No. 1 of this series. The alcohol was evaporated from the resulting mixture under an absolute pressure of 5 mm. of Hg.

The results obtained on these samples in the five co-operating laboratories are given in the table. The figures tabulated represent individual analyses and in one case (Laboratory No. 1, 2nd series), three different analysts made the determinations. Averages, deviations from the average, and average deviations are given in the table. In calculating the averages, those analyses differing by more than 100 ppm. from the average were dropped.

An inspection of the data shows that the F. F. A. method is entirely unreliable for the determination of amounts of soap of the order contained in these samples. It was the general opinion of the members of the committee that this method should not be considered further.

The members of the committee were also of the opinion that the Durst ashing method was unsatisfactory mainly because of the difficulties involved in quantitatively ashing a large amount of oil. With care, however, good results can be obtained with this method.

The alcohol extraction method gave low results and failed to show the 100 ppm. of soap added to sample No. 2 of the second series. The per cent average deviation was

greater for this method than for either the Durst or Modified Durst methods in all cases except one.

The Durst and Modified Durst methods apparently gave the best results. The modified method has the advantage of being much less laborious than the original one and appears to give more reproducible results.

In view of the data presented herein, the committee does not recommend the adoption of any of these methods as official or tentative methods of the Society but does recommend that the co-operative work be continued for at least another year particularly on the Durst HCl extraction method, the Durst method as modified by R. C. Stillmann, and the alcohol extraction method.

REFERENCES

1. R. Durst: Oil and Soap 12, 271-3.
2. Spielman; Joyner; Lappen and Stillman: ibid 14, 153-4.
3. Spielman; Joyner; Lappen and Stillman: ibid 13, 177.

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FIRST SERIES—Sample No. 1

	Durst Ashing Soap P.P.M.	Dev. from Avg.	Durst Soap P.P.M.	Dev. from Avg.	Modified Durst Soap P.P.M.	Dev. from Avg.	Alcohol Extraction Soap P.P.M.	Dev. from Avg.	F.F.A. Soap P.P.M.	Dev. from Avg.
Laboratory No. 1	25	9.7	13	13	25	2.2	25	5.6	74	39.4
	21	5.7	22	4	29	6.2	27	7.6	4	30.6
Laboratory No. 2	..	...	..	..	17	5.8	24	4.6	..	...
	..	...	..	..	20	2.8	12	7.4	..	...
	..	...	..	..	27	4.2	..	..	..	...
	..	...	..	..	28	5.2	..	..	..	...
Laboratory No. 3	..	...	62.5	36.5	..	...	30.3	10.9	65.9	31.3
	..	...	43.3	17.3	..	...	37.2	17.8	29.1	5.5
Laboratory No. 4	0	15.3	7.5	18.5	18	4.8	0	19.4	0	34.6
	..	...	7.5	18.5	18	4.8	0	19.4	..	...
Average	15.3	10.2	26.0	18.0	22.8	4.5	19.4	11.6	34.6	28.3
	(66.6%)		(69.2%)		(19.7%)		(59.8%)		(81.8%)	

FIRST SERIES—Sample No. 2

Laboratory No. 1	72	8	72	5.9	72	21.7	48	10.6	89	24
	74	10	76	9.9	77	26.7	46	8.6	58	7
Laboratory No. 2	..	..	..	..	31	19.3	30	7.4	..	...
	..	..	..	..	34	16.3	30	7.4	..	...
	..	..	..	..	47	3.3	..	...	..	...
	..	..	..	..	45	5.3	..	...	..	...
Laboratory No. 3	..	..	78.5	12.4	..	...	45.2	7.8	59.8	5.2
	..	..	78.1	12.0	..	...	54.3	16.9	67.3	2.3
Laboratory No. 4	46	18	46	20.1	48	2.3	22.9	14.5	51	14
	..	..	46	20.1	48	2.3	22.9	14.5	..	...
Average	64.0	12	66.1	13.4	50.3	12.1	37.4	11.0	65.0	10.5
	(18.7%)		(20.3%)		(23.0%)		(29.4%)		(16.2%)	

SECOND SERIES—Sample No. 1

	Durst Ashing Soap P.P.M.	Dev. from Avg.	Durst Soap P.P.M.	Dev. from Avg.	Modified Durst Soap P.P.M.	Dev. from Avg.	Alcohol Extraction Soap P.P.M.	Dev. from Avg.	F.F.A. Soap P.P.M.	Dev. from Avg.
Laboratory No. 1	100	26.8	252*	..	150	25.2	112	35.4	289*	...
	135	8.2	249*	..	158	33.2	87	10.4	..	...
	121	5.8	95	0	131	6.2	55	21.6	..	...
	156	29.2	143	48	121	3.8	33	43.6	..	...
	122	4.8	343*	..	119	5.8	121	44.4	284*	...
	248*	...	407*	..	115	9.8	164	87.4	..	...
Laboratory No. 2	...	...	..	..	102	22.8	43	33.6	93	20.6
	...	...	..	..	107	17.8	40	36.6	..	...
Laboratory No. 3	...	...	81.1	13.9	...	...	30.3	46.3	59.1	13.3
	...	...	71.1	23.9	...	...	..	..	...	...
Laboratory No. 4	...	...	90	5	135	10.2	45.8	30.8	55.9	16.5
	...	...	90	5	120	4.8	124	47.4	77	4.6
	...	...	..	..	120	4.8	64	12.6	77	4.6
	...	...	..	..	120	4.8	..	..	..	...
Average	126.8	15.0	95.0	16.0	124.8	12.4	76.6	37.5	72.4	11.9
	(11.8%)		(16.8%)		(9.9%)		(49.0%)		(16.4%)	

SECOND SERIES—Sample No. 2

Laboratory No. 1	291	75.3	260	94.8	260	57.7	102	.9	247*	...
	271	55.3	262	96.8	259	56.7	103	.1	..	...
	121	94.7	126	39.2	64*	...	46	56.9	..	...
	121	94.7	133	32.2	92*	...	53	49.9	..	...
	248	32.3	172	6.8	119	83.3	127	24.1	238*	...
	242	26.3	127	38.2	..	...	95	7.9	244*	...
Laboratory No. 2	...	...	..	..	169	33.3	76	26.9	85	14.9
	...	...	..	..	153	49.3	79	23.9	..	...
Laboratory No. 3	...	...	91.5	73.7	..	...	74.4	28.5	67.2	32.7
	...	...	88.4	76.8	..	...	57.2	45.7	59.0	40.9
Laboratory No. 4	...	...	196	30.8	182	20.3	90	12.9	39	60.9
	...	...	196	30.8	182	20.3	64	38.9	58.5	41.4
	...	...	..	..	210	7.7	..	..	..	...
	...	...	..	..	215	12.7	..	..	..	...
Laboratory No. 5	...	...	..	..	210	7.7	170	67.1	130	30.1
	...	...	..	..	240	37.7	180	77.1	170	70.1
	...	...	..	..	229	26.7	170	67.1	150	50.1
	...	...	..	..	..	...	160	57.1	140	40.0
Average	215.7	63.1	165.2	52.01	202.3	34.5	102.9	36.6	99.9	42.8
	(29.3%)		(31.5%)		(17.1%)		(35.6%)		(43.2%)	

*Samples eliminated—more than 100 P.P.M. from average.