SIMPLIFICATION OF CONTINUOUS EXTRACTION METHOD FOR THE DETERMINATION OF UNSAPONIFIABLE MATTER

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Abstract

The simplification consists of eliminating from the procedure for determining unsaponifiable matter, the washing of the petroleum ether extract. A procedure for eliminating this washing is proposed. Tabulated results show that accuracy is not impaired.

LATE in 1938, Wood and Roschen[1] published a method incorporating continuous extraction for the determination of unsaponifiable matter in greases and tallows. While this method eliminated many of the manipulations and much of the handling of the Official or shakeout[2] method of determination, the simplification proposed by these authors had only to do with the extraction, the remaining parts of the Official method being retained intact. Hence, the washing with 10% alcohol, filtering, drying, weighing of the unsaponifiable material, and titrating the fatty acids extracted from the soap solution in the washing process were retained.

This paper will show how the washing with 10% alcohol and titration of the fatty acids resulting from hydrolysis can be eliminated, thus further simplifying the method, with consequent saving in manipulative time, and with no sacrifice in accuracy.

THEORY

During the extraction with petroleum ether, some of the soap from the saponification tube is carried over as emulsion with the petroleum ether extract. The purpose of washing the extract with 10% alcohol in the Official Method is to remove this soap, in order that the extract may be readily filtered.

The presence of the fatty acid in the final extract is due to the fact, that soap, in aqueous solution, hydrolyzes according to the following equation:

$$RCOOK + H_2O = RCOOH + KOH$$

The resulting fatty acid and KOH are in equilibrium with the unhydrolyzed soap. Since, during the saponification, there is such an excess of KOH that the equilibrium is displaced to the left (i.e. in favor of the reaction products RCOOK and H_2O), there is negligible extraction of the fatty acid. However, if the washing procedure is carried out, the wash water will be relatively free of KOH, hydrolysis of the soap carried over mechanically during the extraction will take place, and the fatty acid will be extracted, taken up in the petroleum ether extract and carried into the final filtrate. It then must be titrated and the unsaponifiable residue corrected for the amount of fatty acid found. Since there is no appreciable hydroysis during extraction of the highly alkaline soap solution, and since such hydrolysis as does occur probably arises in the 10% alcohol washes, elimination of these washes should eliminate the fatty acid correction.

If the extraction is made by the Official or shakeout method, the volume of soap carried over is so great that filtering is impossible without washing. With continuous extraction the volume of soap is so greatly reduced that washing may be eliminated. Hence, if the petroleum ether extract is evaporated off directly after extraction and without any washing and the residue dried, this residue can then be taken up in petroleum ether, filtered into a tared beaker and weighed as unsaponifiable matter without a correction. Thus, the 10% alcohol wash, titration of the fatty acid, and correction are all eliminated, greatly simplifying the present method.

Such a simplification was tried and the results of these trials are recorded in this paper.

The simplification followed the method of Wood and Roschen[1] in saponification and extraction. The sample was weighed into a weighing boat, transferred to a tube, and saponified for one hour. The tube was then filled to the mark and extracted for two and one-half hours.*[1]

	10% Alcohol Washing Procedure		Proposed Procedure		
	% Unsaponifiable (Corrected)	Titratable Fatty Acids	% Unsaponifiable (Uncorrected)	Titratable Fatty Acids	Difference
GREASE	2.58	0.12	2.60	0.05	+0.02
	2.33	0.07	2.35	0.02	+0.02
	2.51	0.16	2.43	0.01	—0.09
	2.77	0.13	2.69	0.04	—0.08
	2.42	0.17	2.36	0.01	—0.06
	2.81	0.14	2.80	0.02	—0.01
	1.44	0.06	1.44	0.03	0.00
	2.21	0.10	2.04	0.03	—0.17
	2.17	0.04	2.24	0.00	+0.07
	1.46	0.17	1.45	0.00	—0.01
	0.82	0.07	0.87	0.01	+0.05
	1.68	0.16	1.75	0.02	+0.07
	1.64	0.10	1.77	0.02	+0.13
	1.50	0.14	1.51	0.04	+0.01
	2.41	0.12	2.40	0.03	—0.01
	1.79	0.18	1.77	0.03	—0.02
	1.23	0.12	1.29	0.03	+0.06
	1.85	0.05	1.67	0.00	—0.18
	1.25	0.04	1.24	0.00	—0.01
	1.64	0.10	1.77	0.02	+0.13
TALLOW	1.86	0.06	1.75	0.00	—0.11
	1.45	0.02	1.50	0.03	+0.05
	1.27	0.03	1.33	0.00	+0.06
	1.51	0.18	1.65	0.00	+0.14
	1.57	0.15	1.72	0.03	+0.15
	1.74	0.09	1.64	0.00	—0.10
	1.11	0.16	1.09	0.03	—0.02
	2.05	0.05	2.13	0.01	+0.08
	1.30	0.07	1.37	0.02	+0.07
	0.99	0.09	0.99	0.02	0.00
OLIVE OIL FOOTS	2.16	0.20	2.17	0.03	+0.01
BUTTER	0.44	0.09	0.47	0.03	+0.03
Average *Difference*					0.06
Maximum Difference					0.18

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*The addition of a few grains of *acid* washed dry sand to the Soxhlet flasks reduces irregular boiling, makes the extraction go much more smoothly, and is therefore recommended.

Subsequent to the extraction phase of the Wood-Roschen method, the following procedure was used for recovering the unsaponifiable matter from the petroleum ether solution.

PROCEDURE

Transfer the Soxhlet flasks containing the petroleum ether extract to a steam bath, and evaporate to dryness under filtered air. Transfer to 101° C. oven and dry for fifteen minutes. Remove the flasks and allow them to cool. Take up the unsaponifiable matter in 50 ml. of petroleum ether and filter the solution into a tared beaker, taking care to wash the filter paper free of unsaponifiable matter. Transfer the beaker containing the filtrate to a steam bath, evaporate to dryness, and dry to constant weight in an oven at 101° C. Calculate the weight of the residue directly to percentage unsaponifiable.

DISCUSSION

Results obtained with this procedure, as compared with those obtained using the regular 10% alcohol washing procedure, are shown in the table. It will be noted that the correction for fatty acids in the extract has fallen to negligible amounts in all cases where the proposed procedure was used. The values given for unsaponifiable matter in this tabulation are corrected for fatty acids in the case of the 10% alcohol washing procedure and uncorrected for these fatty acids in the proposed procedure.

It will be noted that these two groups of values are in good agreement, the maximum divergence being 0.18%.

It is felt that the modified procedure for unsaponifiable matter proposed in this paper will considerably simplify the method described by Wood and Roschen[1] and result in considerable economy in time required for the determination.

REFERENCES

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2. Methods of Fat Analysis Committee of Am. Oil Chemists Soc. and Am. Chem. Soc., P. 30-30A.

Fat From Locusts

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THE locust, a name common to several orthopterous insects, is divided into two families: 1. Locustariae, embracing grasshopper-like species which have very long, slender antennae and four-jointed tarsi. 2. Acyrydii, embracing very numerous species which have a large head, short and stout antennae, very strong hind legs, and three-jointed tarsi. Locusts are found in almost all parts of the world, but they abound chiefly in tropical and subtropical countries, and most of all in Arabia, Africa, and parts of South America where the Migratory Locust does immense injury to vegetation, literally devouring everything green.

Not only are live locusts a menace to man and his crops, but after the death of an army of locusts, the putrefaction which arises from their inconceivable number is so great that it has been the cause of the depopulation of whole districts of country.

However, the locust has been found of some use in spite of its general undesirability. Even in Biblical times we find mention in the Bible of locusts being used as a common food. Locusts are still eaten in many countries, roasted, or fried in butter. They appear, it is stated, in the markets of Arabia and Egypt and are even exported as an article of commerce.

Only very recently have locusts been used as a commercial source of fat, but as long ago as 1887 William K. Kedric, an American, isolated oil from the American locust. In 1893, Dubois extracted the oil from the locust eggs during a locust invasion of Algeria. This oil, he described as resembling egg oil, having a good flavor when freshly extracted but rapidly increasing in acidity, and acquiring the odor of a very sharp codliver oil. Apparently this oil from the eggs of locusts was not extracted in commercial quantities and was not put to any use.

Recently we received a sample of locust fat extracted from adult South American locusts. This sample was dark brown in color, had about the consistency of cottonseed fatty acids, and had a rank, pungent odor. It was a fairly clean fat having about 0.01% insoluble impurities and 0.92% moisture. The chemical and physical characteristics were found to be as follows:

Characteristics of Locust Fat

Moisture	0.92%
Insoluble Impurities	0.01%
Unsaponifiable Matter	1.83%
Free Fatty Acids (Oleic)	27.7 %
Titre	39.0° C.
Color (FAC)	45
Color (Lovibond-½" cell)	250 Yellow-72 Red
Total Fatty Acids (Pet. Ether)	92.5 %
Iodine Number (Wijs)	65.2
Saponification Number	191.4
Iodine Number Fatty Acids	68.2
Saponification Number Fatty Acids	194.5
Unsaponifiable Matter Fatty Acids	1.4 %
Solid Fatty Acids (Lead Salt Ether) uncorrected	36.4 %
Liquid Fatty Acids (Lead Salt Ether) uncorrected	54.7 %
Iodine Value (Wijs) Solid Acids	13.45
Iodine Value (Wijs) Liquid Acids	100.9
Thiocyanogen Value Solid Acids	11.5
Thiocyanogen Value Liquid Acids	78.7
Solid Fatty Acids (Corrected)	31.5 %
Liquid Fatty Acids (Corrected)	59.5 %
Specific Gravity at 50° C.	0.8948

Assuming the absence of linolenic acid in this sample, the analysis indicated that the fat contained the following percentages of fatty acids:

Oleic Acid	43.1%
Linoleic Acid	16.4%
Saturated Acids	31.5%
Unsaponifiable Matter	1.4%