MODIFIED KERR-SORBER METHOD

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The Association of Official Agricultural Chemists, during 1924, studied the determination of unsaponifiable matter in fats and grease by three methods: the Kerr-Sorber method[1], a modified A. O. A. C. method[2], and the method of the Committee on Analysis of Commercial Fats and Oils of the American Chemical Society[3]. Several collaborators found considerable quantities of free fatty acids or acid soaps in the residues obtained by the Kerr-Sorber method. On the other hand, only small quantities of these acid substances were found in the residues from the Committee method by one of the collaborators. Since then, these observations have been confirmed by the authors. The titratable acidity of the residues by the Kerr-Sorber method was found to range from 0.5–1.1 ml. of 0.1 *N* alkali as compared to 0.05–0.15 ml. by the Committee method. It is evident, therefore, that considerable hydrolysis of the soap takes place in the Kerr-Sorber method during the washing of the ether with the large volumes of water.

The chemical literature discloses a previous method for the determination of unsaponifiable matter that provides against the extraction of fatty acids along with the unsaponifiable matter. Thaysen[4], in a study of the determination of cholesterin and chalesterin esters, proposed a method quite similar to that of Kerr and Sorber for the extraction of these substances from lipoids. In this method the soap is washed out of the ether solution of the unsaponifiable matter with dilute alkali. This procedure tends to avoid hydrolysis of the soaps and the consequent extraction by the ether of the derived fatty acids. The concentration of the alkaline wash solution is not specified by Thaysen. Fex[5] successfully employs this particular procedure of Thaysen for the extraction of unsaponifiable matter from body organs.

Many experiments were made in attempting to overcome the hydrolysis of the soap and the subsequent extraction of free fatty acids in the case of the Kerr-Sorber method. The ether-soap solution was washed first with three successive 100 ml. portions of dilute potassium hydroxide solution ranging in concentrations from 0.1–1.0 normality. The ether then was washed with successive 30 ml. portions of water to remove the alkali. The concentration that appeared to be the most suitable for the purpose was a 0.2 *N* potassium hydroxide solution. Results on four samples of oils and greases analyzed in this manner are shown in the table. The titratable acidity obtained in these instances was negligible. Some comparative results by the Committee method also are given.

[1] The Cotton Oil Press, 1924, 7: 40; *J. Asso. Official Agr. Chemists*, 1924, 8: 90.
[2] *J. Assoc. Official Agr. Chemists*, unpublished.
[3] *Ibid.*, 1924, 8: 85.
[4] *Biochem. Z.*, 1914, 62: 89.
[5] *Ibid.*, 1920, 104: 82.

UNSAPONIFIABLE MATTER

Analysts	Modified Kerr-Sorber Method	Committee Method 5 Extractions	Committee Method 7 Extractions	Committee Method 9 Extractions
		SAMPLE A		
	per cent	per cent	per cent	per cent
G. S. Jamieson	0.20	0.18	0.20	....
	0.20		0.22	
W. F. Baughman	0.20	....	....	....
	0.20			
L. H. Bailey	0.17	....	....	....
	0.18			
		SAMPLE B		
G. S. Jamieson	0.55	0.55	0.60	....
	0.56	0.57	0.61	....
W. F. Baughman	0.54	....	....	....
	0.58			
L. H. Bailey	0.56	....	....	....
	0.53			
		SAMPLE C		
G. S. Jamieson	1.32	0.97	1.13	....
	1.34	0.99	1.19	
W. F. Baughman	1.34	0.98	1.14	1.34
	1.29		1.15	1.40
L. H. Bailey	1.22	....	....	....
	1.26			
Dorothy Paine, Bureau of Chemistry, Washington, D. C.	1.21	....	....	....
	1.28			
	1.29			
	1.32			
		SAMPLE D		
G. S. Jamieson	1.89	1.79	1.91	....
	1.93	1.80	1.93	
	1.96			
W. F. Baughman	1.98	1.76	1.93	....
	2.00	1.82	2.00	
L. H. Bailey	1.92	....	....	....
	2.02			
Dorothy Paine	1.94	....	....	....
	1.98			
	2.03			
Raymond Hertwig	1.97	....	....	....
	2.00			
	2.02			

The results indicate that a slight modification of the Kerr-Sorber method, involving the washing of the soap out of the ether solution of the unsaponifiable matter with 0.2 *N* potassium hydroxide solution, practically removes the only known objection raised to this splendid method, namely, the extraction of a small quantity of fatty acids with the unsaponifiable matter. A description of this modified method follows:

Reagents and Apparatus

(a) Concentrated potassium hydroxide solution.—100 grams of potassium hydoxide dissolved in 100 ml. of water.

(b) Dilute potassium hydroxide solution, approximately 0.2 *N*.—

11.2 grams of potassium hydroxide dissolved in 1000 ml. of water.

(c) Ethyl alcohol.—Approximately 95 per cent by volume.

(d) Ethyl ether.—U. S. P.

(e) Phenolphthalein solution.—1 gram of phenolphthalein dissolved in 100 ml. of alcohol.

Apparatus

(a) Separatory funnel.—500 ml. capacity, ether-tight. The glass connections are lubricated with water.

(b) Erlenmeyer flask or beaker-flask for saponification.—100-200 ml. capacity.

(c) Erlenmeyer flask or beaker-flask.—250 ml. capacity.

Procedure

Accurately weigh about 5 grams of sample into the saponification flask. Add 30 ml. of the alcohol and 3 ml. of the concentrated potassium hydroxide solution. Place a small, short-stemmed funnel in the neck of the flask to serve as a condenser. Boil gently on the steam bath for about 20 minutes or until complete saponification occurs. Cool to about 30°C., add 50 ml. of ether, mix, and transfer to the separatory funnel. Rinse the flask with two successive 50 ml. portions of ether, add to the separatory funnel, and mix thoroughly. Wash the saponification flask with 100 ml. of the dilute potassium hydroxide solution and pour into the separatory funnel in a slow, steady stream. Rotate the funnel very gently to secure better contact of the solutions but do not shake. (Shaking at this stage brings about stubborn emulsions.) Allow the liquids to separate completely and then slowly draw off as much of the soap solution as possible. Do not draw off any layer of emulsion that may be formed. Keep the volume of the ether at about 150 ml. by replacing that dissolve by the wash solutions. Further treat the ether solution with two successive 100 ml. portions of the alkaline wash solution in the manner described previously. Add 30 ml. of water to the ether and rapidly rotate the liquid layers. When the layers have separated completely, draw off the water. Repeat this treatment until the washings are free from alkali, as shown by testing with phenolphthalein. Three washings usually suffice. Transfer the ether solution quantitatively through a pledget of cotton in the stem of a funnel to the weighed 250 ml. Erlenmeyer flask or beaker-flask. Before weighing the flask dry it in an oven at 100°C., and then allow it to stand in the air to constant weight. Distil off the ether and dry the flask and residue at 100°C. until no further loss in weight occurs. Allow the flask with unsaponifiable matter to come to equilibrium with the atmosphere before weighing. Deduct from the weight of the unsaponifiable matter any blank obtained from the reagents used.