Analysis of Traces of Anionic Detergents in Oils and Fats

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ABSTRACT

A method to analyze oils and fats for anionic detergents, mainly sodium lauryl sulphate (NaLS), has been developed. After extracting the detergent from the oil, a chloroform-soluble complex with methylene blue is formed, and the concentration of this complex is determined spectrophotometrically. The method was found suitable for oils and fats containing 0.05 to 5.0 mg NaLS per kg. The analysis can only be used to assess fully refined oils and fats because partly refined and commercially available products may contain minor components and emulsifiers also solubilizing methylene blue into chloroform.

INTRODUCTION

Fats, fatty acids and fatty alcohols can be separated on a technical scale into fractions with different melting points by mixing the partly crystallized material with an aqueous detergent solution usually containing sodium decyl or lauryl sulfate and inorganic salts such as Na_2SO_4, $MgSO_4$ or $Al_2(SO_4)_3$ (1). After mixing, the crystals enter into the aqueous phase, and the olein is obtained by centrifugation. Then the remaining aqueous phase is heated, and the melted stearin is obtained by a second centrifugation process.

The fractions obtained usually contain residual detergent which, particularly in the case of edible fats, must be removed by washing and refining. This implies that a sensitive analytical method is required for product control.

In aqueous medium, anionic detergents can be determined gravimetrically (2-4), volumetrically (5-15), or spectrophotometrically (16-21), the latter methods being the most sensitive ones. We have developed a method for oils and fats, starting from a standard German method (22). This method is based on the formation of a chloroform-soluble complex of detergent and methylene blue in a stoechiometric ratio. The detergent in the oil is extracted with water or with water/ethanol, and the extract is acidified with H_2SO_4 to convert fatty acid soaps, if present, into fatty acids. As these compounds may disturb the analysis, they are extracted with chloroform. The aqueous extract containing the detergent is neutralized, and after formation of the complex by the addition of methylene blue solution, the detergent concentration is determined spectroscopically.

EXPERIMENTAL

Standard Solutions and Chemicals

Methylene blue solution, neutral: 0.35 g methylene blue is dissolved in distilled water and diluted to 1 l.

Methylene blue solution, acid: 0.35 g methylene blue is dissolved in 500 ml distilled water and 6.5 ml concentrated H_2SO_4 (density = 1.84) is added after which the solution is made up to 1 l.

The methylene blue solutions should stand for 24 hr at least before use; they are purified by shaking with chloroform.

Phosphate solution: 12.52 g $Na_2HPO_4 \cdot 2H_2O$ is dissolved in 500 ml distilled water; pH is adjusted to 10 by adding ca. 3 ml NaOH (0.5 mol/l), after which the solution is made up with distilled water to 1 l.

Detergent solution 1:1.0 g detergent of known composition is dissolved in 1 l water.

Detergent solution 2:10 ml of detergent solution 1 is made up to 1 l (detergent concentration 10 μg/ml).

Detergent solution 3:50 ml of detergent solution 2 is made up to 500 ml (detergent concentration 1 μg/ml).

Chloroform, ethanol, H_2SO_4 (0.05 mol/l) and NaOH (0.5 mol/l) analytical grade. Pure NaLS (ex BDH, England) and laboratory grade methylene blue (ex Noury-Baker N.V., Netherlands) were used. All fats used in model systems were fully refined and purified by stirring with Al_2O_3.

Calibration

Amounts of the standard detergent solutions containing 20, 50, 100, 150 and 200 μg of detergent are each added to 100 ml quantities of distilled water in 250 ml separating funnels. Ten ml sodium phosphate solution, 5 ml neutral methylene blue solution, and 15 ml chloroform are added to each funnel; funnels are shaken gently for 1 min.

After separation, the chloroform layer is run off into another separating funnel containing 100 ml water and 5 ml acid methylene blue solution. This mixture is also shaken for 1 min. After separation, the chloroform layer is filtered through a funnel plugged with cotton wool into a calibrated flask. The cotton wool plug should be moistened with chloroform. The extraction steps are repeated twice with 10 ml chloroform, and the cotton wool plug is washed with chloroform. Finally the total chloroform extract is made up to 50 ml, and the optical density is measured in a 1 cm cell at 650 nm in comparison with a blank, treated in the same way. The calibration curve is obtained by plotting the optical density as a function of the weight of detergent; a straight line passing through the original should be obtained.

TABLE I

Recovery of NaLS from Peanut Oil

NaLS		
	recovered	
added (mg/kg)	(mg/kg)	%
5.0	4.0[a]	80
2.0	1.7[a]	85
1.0	0.82	82
0.70	0.70	100
0.50	0.41[a]	82
0.25	0.22[a]	88
0.20	0.16	80
0.10	0.10	100

[a]Extraction with water.

TABLE II

Average Extraction Yields of NaLS from Various Fats and Oils

Oil or fat	NaLS added/(mg/kg)	Recovery average/%
Peanut	0.05 to 5.0	87
Palm kernel stearin	0.25	102
Sunflower oil	0.1 to 1.0	74[a]
Cottonseed oil	0.1 to 1.0	89[a]
Palm oil fraction	0.1 to 1.0	88[a]

[a]Labeled NaLS.

TABLE III

Standard Deviation of the Analysis

Oil or fat	NaLS level (mg/kg)	Number of determinations	Standard deviation
Peanut	1.1	7	0.18
Palm kernel stearin	0.25	8	0.05
Groundnut oil	0.10	6	0.03

Extraction of Detergent from the Oil

Two hundred g of the oil is weighed into a 500 ml stoppered conical flask and 50.0 ml distilled water or water/ethanol (1/1; v/v) is added from a pipette. The flask is heated carefully to 80 C and shaken or stirred vigorously for 1 hr. If the fat solidifies during this procedure, the flask is again heated before mixing is continued.

After shaking or stirring, the flask is allowed to stand in a bath of hot water for 1 hr to break up any remaining emulsion. Then the mixture is centrifuged at 3000 g for 5 min, after which the aqueous phase is isolated.

TABLE IV

Recovery of NaLS from Soap-Containing Peanut Oil after Extraction with Water/Ethanol (1/1, v/v) and Soap Removal

NaLS added (mg/kg)	Potassium oleate added/(mg/kg)	NaLS recovery (mg/kg)	NaLS recovery %
2.00	0	1.67	84
2.00	200	1.55	78
2.00	600	1.85	93
2.00	1000	1.84	92
2.00	2000	1.88	99
0	1000	0.00	---
0.10	1000	0.10	100
0.30	1000	0.31	103
0.50	1000	0.53	106
1.00	1000	1.09	109
1.50	1000	1.54	103

TABLE V

NaLS Content of Detergent-Fractionated Palm Kernel Olein and Stearin after Various Stages of the Refining Process

Refining stage		Concentration of NaLS/(mg/kg) olein	stearin
Crude,	after fractionation	7.5	25
	after lye neutralization	0.46	3.3
	after bleaching with earth	0.05	0.15
	after deodorization (4 hr, 180 C)	not detectable	not detectable

TABLE VI

Analysis of Peanut Oil Containing Emulsifiers and NaLS (5 mg/kg)

Emulsifier	NaLS recovered (mg/kg)
1% Tween[a] 20	3.5
1% Tween 60	3.3
1% Tween 80	3.4
1% Tween 85	3.9
1% Myrj[b] 45	4.3
1% Myrj 52	3.7
1% Span[c] 20	5.5
1% Span 40	5.4
1% Span 80	5.3
0.1% Soy lecithin	5.4
0.05% Soy lecithin	5.5

[a]Polyoxyethylene sorbitan esters ex Atlas.
[b]Polyoxyethylene esters ex Atlas.
[c]Sorbitan esters ex Atlas.

Determination of Detergent in the Aqueous Extract

Twenty-five ml of the extract is added to 50 ml water in a separating funnel, and 20 ml H_2SO_4 (0.05 mol/l) is added. This solution is extracted twice with 15 ml chloroform to remove fatty acids which may be present. After the solution is neutralized with NaOH (0.5 mol/l), 10 ml sodium phosphate solution, 5 ml neutral methylene blue solution and 15 ml chloroform are added; the separating funnel is shaken gently for 1 min. The procedure is continued as is described for the determination of the calibration curve. The weight of detergent (μg) in 25 ml of the extract is then obtained by reference to the calibration curve; dividing this figure by 100 gives the level of detergent in oil in mg/kg.

Testing of Method

The method has been tested by recovery experiments in which known amounts of sodium lauryl sulphate (NaLS) were added to samples of different oils and fats. Also samples of different refining stages of a detergent-fractionated palm kernel olein and stearin were analyzed.

RESULTS AND DISCUSSION

Basically the extraction of the detergent from the oil can be done with water, but then occasionally too low yields are obtained. This may be due to the formation of a very fine W/O emulsion which remains stable on subsequent heating and centrifugation. In this way an appreciable amount of detergent may be adsorbed onto the W/O interface and be retained in the oil. In such cases the extraction yield can be improved considerably by using water/ethanol (1/1; v/v).

Extraction yields were sometimes found to depend on the kind of fat. When NaLS is extracted from fully refined groundnut oil, the extraction yield is between 80 and 100% (Table I). For palmkernel stearin containing 0.25 mg NaLS per kg, an extraction yield between 88 and 118% was found when water was used. For sunflower oil, cottonseed oil and a palm oil fraction (m.p. 28 C), NaLS recovery was measured using labeled NaLS. The extraction yield was determined by measuring the radioactivity of the oil before and after aqueous extraction and centrifugation. Average yields are summarized in Table II.

To characterize the precision of the determination, a coefficient of variation of 10% was calculated from the data in Table I. The reproducibility of the method was also tested (Table III); the results show that less accurate values are found at the lowest NaLS concentrations. Values lower than 0.05 mg NaLS per kg were found to be completely unreliable.

When fats that are not fully refined are analyzed, fatty acid soaps remaining after lye neutralization may interfere. The amount of methylene blue present in the alkaline solution corresponds with 13.5 mg NaLS per kg fat and with 15.0 mg fatty acid soap (as potassium oleate) per kg fat. In a fat containing 2 mg NaLS per kg, amounts of more than 20 mg fatty acid soap per kg influence the

TABLE VII

Apparent Concentration of NaLS (mg/kg) Detergent-Free Peanut Oil Containing Additives

Centrifugal force		Additive		
aqueous extract	final $CHCl_3$ phase	1% Krill 41	1% Span 40	1% Famodan TS
3000 g	---	0.25	0.40	0.15
10000 g	---	0.27	1.16[a]	0.08
10000 g	10000 g	0.24	1.52[a]	0.13

[a]Turbid.

analysis due to competition in complex formation. As in practice, 50 to 400 mg soap per kg fat may be present after neutralization, a soap removal step was introduced in the standard procedure; some results are given in Table IV.

Table V shows the detergent (NaLS) content of palm kernel olein and stearin obtained from a separation with an aqueous detergent solution. In the final products no detergent could be shown, as the last traces were hydrolyzed during deodorization.

Commercial fat fractions like shortenings and cocoa butter substitutes may contain emulsifiers, while crude fats may contain phosphatides. Therefore, the method was tested on peanut oil containing 5 mg NaLS per kg and polyoxyethylene sorbitan esters, polyoxyethylene esters, sorbitan esters, or crude soybean lecithin. The results are given in Table VI. As some results with samples containing sorbitan ester or lecithin were found to be rather high, detergent-free samples containing lecithin, Span 40 (sorbitan monopalmitate, ex Atlas), Krill 41 (sorbitan tristearate, ex Croda Food Ltd) or Famodan TS (sorbitan tristearate, ex Grindsted Vaerket) were analyzed (Table VII). During the analysis of the sample containing lecithin, considerable emulsion problems were encountered in particular during the extraction of the chloroform-soluble methylene blue complex from the alkaline solution; centrifugation at 10,000 g was necessary to break the emulsion. On further analysis, the measured optical density suggested the presence of 0.97 mg NaLS per kg. After the aqueous extraction, the centrifugal force was increased, and even the final solution of the methylene blue complex was centrifuged under a cover of acid methylene blue solution in order to reduce any emulsified methylene blue. These precautions did not improve the results, and as no anionics are expected to be present in the sorbitan ester, it must be assumed that some methylene blue is solubilized into chloroform by the action of the emulsifiers.

REFERENCES

1. Solms, J., "Functional Properties of Fats in Foods," Forster Publishing Ltd, Zürich/Schweiz, 1973, pp. 198-200.
2. Marron, T.V., and T. Schifferli. J. Ind. Eng. Chem. Anal. 18:49 (1946).
3. Blank, E.W., Soap Chem. Spec. 34:41 (1958).
4. Jenkins, J.W., and K.O. Kellback, Anal. Chem. 31:1056 (1959).
5. Hartley, G.S., and D.F. Rumicles. Proc. Roy. Soc. London 168:420 (1938).
6. Ban, T., J. Oliver, and W.V. Strubbings. J. Soc. Chem. Ind. 67:45 (1948).
7. Harper, W.J., P.R. Elliker, and W.K. Mosely. Soap San. Chem. 24:159, 161, 163 (1948).
8. Kupfer, W., III Intern. Kongr. Grnsfl. act Stoffe 3:62 Univ. Drückerei Mainz (1960).
9. Epton, S.R., Nature 160:795 (1947).
10. Epton, S.R., Trans. Far. Soc. 44:226 (1948).
11. Weatherburns, A.S., JAOCS 28:233 (1951).
12. Smith, T.D., and J. Glazer, Nature 169:479 (1952).
13. Lewis, G.R., and L.K. Herndon, Sewage and Wastes 24:1456 (1952).
14. Heinerth, E., Fette Seifen Anstrichm. 72:335 (1970).
15. Report of the Commission International d'Analyses Tenside 4:292 (1967).
16. J.H. Jones, J. Assoc. Off. Agric. Chem. 28:398 (1945).
17. Wallin, G.R., Anal. Chem. 22:616 (1950).
18. Moore, W.A., and R.A. Kolbesen, Ibid. 28:161 (1956).
19. Longwell, J., and N.D. Maniece, Analyst 80:167 (1955).
20. Abbot, D.C., Analyst 87:286 (1962).
21. Martinez Morene, J.M., and W. Flores Lugne. Grasas y Aceitas pp. 157-159 (1967).
22. Deutsche Einheitsverfahren zur Wasseruntersuchung H 23.la.

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