Technical

A Spectrophotometric Method for Determination of Solid Fat Content of Palm Oil

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ABSTRACT

A new spectrophotometric method has been developed for determining solid fat content (SFC) of crude palm oil based on the different solubilities of the inherent carotenes in the solid and liquid components of the oil. The sample to be analyzed is tempered according to usual procedures and then either filtered or centrifuged to liberate the liquid component (olein). The carotene contents of the palm oil and olein as determined by spectrophotometry are then fitted into an equation to obtain the SFC. The carotenes are apparently insoluble in the solid component of palm oil. The standard deviation of analysis on palm oil samples at 25 C is 0.5% which is almost comparable to that of the wide-line NMR technique. The correlation coefficient of SFC measured by these 2 methods over a range of temperatures is 0.99. The new method can also be used to determine SFC of hybrid palm oil (*Elaeis guineensis* X *E. oleifera*) and different palm oil-stearin blends.

INTRODUCTION

Crude palm oil is an orange-red semisolid at normal room temperature. The reddish color is due to the presence of carotenoids, of which α- and β-carotenes are the major components. The carotene content of Malaysian crude palm oil varies from 500 to 700 ppm. However, some hybrid oils of *Elaeis guineensis* x *E. oleifera* have carotene contents of around 1,000 ppm; the oil of the South American Palm *E. oleifera* has even been reported to have over 3,000 ppm of carotenes (1,2).

It has been known that crude palm oil, upon fractionation, normally yields an olein fraction with a slightly higher carotene content than the stearin. This difference in carotene concentrations of the liquid and solid components has provided us the basis for developing a method of determining solid fat content (SFC). Preliminary work had been carried out at the Tropical Product Institute (A.S.H. Ong and N. MacFarlane, private communication).

Theoretically, if the carotene contents of a palm oil and its liquid and solid components at a particular temperature are known, then the SFC of the palm oil can be computed from the following equation:

$$100\,C = (100 - x)\,C_O + x\,C_S \qquad [I]$$

C, C_O and C_S represent the carotene contents of the palm oil, liquid and solid components, respectively, and x is the SFC (%). The carotene contents of the palm oil and its liquid component (olein) can be easily determined by spectrophotometry. The carotene content of the solid component is more difficult to analyze because it is difficult to isolate the pure solid from the palm oil. However, an assumption has been made that, during crystallization of palm oil, the carotenes have remained inthe liquid and whatever carotenes are in the stearin fraction are due to the olein that has been trapped in the solid. The SFC determination is then simplified by letting C_S be zero. Hence, from Equation I:

$$x = 100(C_O - C)/C_O \qquad [II]$$

It is appropriate to mention here that the solid component and stearin of palm oil are not treated as synonymous. The stearin referred to is a product of fractionation of the palm oil and is likely to contain a certain amount of liquid. On the other hand, the olein is regarded as the liquid component which is free of solid.

In this investigation, a wide-line nuclear magnetic resonance (NMR) spectrometer has been used to determine SFC for comparison with the values obtained by the spectrophotometric method.

EXPERIMENTAL

Crude palm oil was melted at 60 C. A small portion of the melted palm oil was removed for carotene content determination by spectrophotometry.

The melted palm oil (5 g) was introduced into a 25-mL round-bottom flask. The flask containing the sample was flushed with nitrogen, stoppered and left to stand at room temperature (ca. 25 C) for 15 min. The sample was chilled in a liquid bath at -20 C for 30 min and then transferred to a water bath kept at the desired temperature, t C, for another 60 min. The crystallized palm oil was vacuum-filtered through a Hirsch funnel lined with Whatman GF/B glass microfibre paper. The temperature of the funnel was maintained at t C by water surrounding it. In the hybrid palm oil (*E. guineensis* x *E. oleifera*, iodine value 73), Whatman GF/C paper was used. The olein filtered through was collected and analyzed for its carotene content.

As an alternative to filtration, the palm oil sample (5 g) was spun in an IEC B-20A high-speed centrifuge to liberate the olein. A medium consisting of 2-propanol and water (56:44 v/v, 10 mL), the density of which was intermediate between those of the liquid and solid components, was added to the tempered palm oil in the centrifuge tube. The contents were then centrifuged at 15,000 rpm (ca. 29,000 g) for 10 min at t C. The olein was removed, dried on a rotary evaporator at 60 C and analyzed.

The tempering procedure (3) suggested by the Palm Oil Research Institute of Malaysia (PORIM) was also tried for the SFC determination of palm oil-stearin blends. The procedure involved melting the sample at 70 C, chilling at 0 C for 90 min and holding at the measuring temperature for 30 min prior to the actual SFC measurement.

Carotenes are known to degrade in the presence of light. Therefore, in the course of experimentation, due care was taken to shield the palm oil samples from light.

Carotene absorption was measured at 446 nm on a

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Unicam SP 8000B ultraviolet recording spectrophotometer. Isooctane was used as solvent and the extinction coefficient of carotene in a 1-cm cell at 1% concentration was taken as 2610.

Crude palm oil for NMR determination was tempered simultaneously and under the same conditions with the samples for the spectrophotometric method. Samples were analyzed on an Mk IIIA Newport Analyser with a WR III sample temperature controller. Olive oil was used as reference. The following instrument conditions were chosen: gatewidth, 1½ gauss; R.F. level, 20 μA; A.F. gain, 350 units; integration time, 32 sec; and sample assembly, 2 mL. The amount of solid was calculated from the formula:

$$SFC\ (\%) = 100[1-(S_tR_{60})/(S_{60}R_t)],$$

where S_t and S_{60} are the NMR readings of the sample, and R_t and R_{60} are NMR readings of the reference oil at t and 60 C, respectively.

RESULTS AND DISCUSSION

Each of the SFC values presented in the tables and graph is the average of duplicate determinations.

Table I compares the SFC values determined by the spectrophotometric and NMR methods over a range of temperatures. The correlation coefficient of 0.99 and 0.97 for the ordinary palm oil and hybrid oil, respectively, indicated that there was a good linear relationship between the values of the 2 methods.

The reproducibility of the 2 methods is shown in Table II. The determinations were performed on 6 different days by the same analysts.

In the spectrophotometric method, filtration of the tempered palm oil was difficult below 15 C. This was partly due to difficulty in maintaining the sample temperature during filtration and also because the olein filtering through was in a very small quantity.

Spectrophotometric determination at temperatures below 15 C was also attempted using a high-speed centrifuge to separate the olein from the palm oil. The results are presented in Figure 1 with the NMR values. A plot of the spectrophotometric and NMR data gave a regression line of Y = 0.852 X + 1.27. The coefficient of correlation was 0.99. However, the precision of the centrifugation technique was comparatively poor. Ten analyses at 25 C on a palm oil sample of 9.4% solid showed a standard deviation of 1.7%.

Zobel et al. have reported in their dye-dilution method (4) that an ultracentrifuge was more suitable in the determination of SFC. With an instrument capable of higher speed and better temperature control than ordinary centrifuges, they were able to obtain a standard deviation of analysis averaging 0.6% for SFC in the range of 15-20%.

The filtration-spectrophotometric technique could be used to analyze palm oil-stearin blends containing varying amounts of solid (Table III). The SFC values measured agreed well with the NMR data.

In the course of this work, it was discovered that the quick low temperature (-20 C) chilling procedure used tends to produce SFC values which fell below the ranges given by PORIM in their survey on palm oil characteristics (3). Table IV shows the SFC values of palm oil-stearin blends determined using the tempering procedure suggested by PORIM. The results were found to be slightly, but significantly, higher than those of the previous procedure.

The experiments performed so far indicated that there was no significant difference between the SFC values of the spectrophotometric and NMR methods, although the spectrophotometric ones tend to give slightly lower values when analyses were performed at low temperatures. This discrepancy might have arisen from several causes. First, during the separation of olein from the tempered palm oil in the proposed method, a part of the solid in the palm oil might have melted because of inadequate temperature control. This could be true especially in centrifugation where there was a tendency for the centrifuge head temperature to rise above the set temperature during spinning because of friction of the moving parts. Another reason could be that, at low temperatures, some of the carotenes were precipitated because of saturation in the olein. Some of the carotenes might also be trapped in the crystallizing solid mass because of their high concentration in the olein.

Nevertheless, the correlation coefficients of almost one between data from the NMR and spectrophotometric techniques, and regression lines which in most cases had gradients close to unity and near zero intercepts, indicate that the earlier assumption of the solid of palm oil being free from carotenes should be justified.

Dilatometry (5) frequently has been said to involve tedious analytical procedures and calculations. Breakage of

TABLE I

Solid Fat Contents of Ordinary Crude Palm Oil and Hybrid Palm Oil (*E. guineensis* × *E. oleifera*) as Measuerd by the Spectrophotometric Technique and Wide-Line NMR

	Solid fat content (%)			
	Palm oil[a]		Hybrid oil[a]	
Temperature (C)	SP[b]	NMR[c]	SP	NMR
40	1.4	1.5	–	–
37.5	3.75	3.35	–	–
35	3.75	4.2	–	–
32.5	5.8	4.8	–	–
30	6.15	6.45	–	–
27.5	7.25	7.75	–	–
25	9.4	9.3	0.75	1.4
22.5	11.2	12.0	–	–
20	13.85	13.3	3.65	2.7
17.5	18.85	19.0	–	–
15	21.05	25.5	6.95	5.9
12.5	–	–	11.2	9.8
10	–	–	8.05	11.25
7.5	–	–	15.65	22.05
5	–	–	19.6	25.05
Regression	Y = 0.861 X + 0.93		Y = 0.695 X + 1.65	
Correlation coefficient	0.987		0.967	

[a]Carotene contents of the palm oil and hybrid oil were 590 and 1140 ppm, respectively.
[b]Ordinate.
[c]Abscissa.

TABLE II

Precision of the Spectrophotometric and Wide-Line NMR Methods

	Solid fat content at 25 C (%)			
	Palm oil A[a]		Palm oil B[b]	
Determination	SP	NMR	SP	NMR
1	13.1	14.1	8.9	9.0
2	13.65	14.05	9.7	9.65
3	13.7	13.95	8.9	9.65
4	13.95	14.5	9.65	9.75
5	14.15	14.5	8.7	9.3
6	14.7	14.9	10.0	9.85
Mean	13.9	14.3	9.3	9.5
Std. dev.	0.5	0.4	0.5	0.3

[a]Iodine value = 51.
[b]Iodine value = 53.

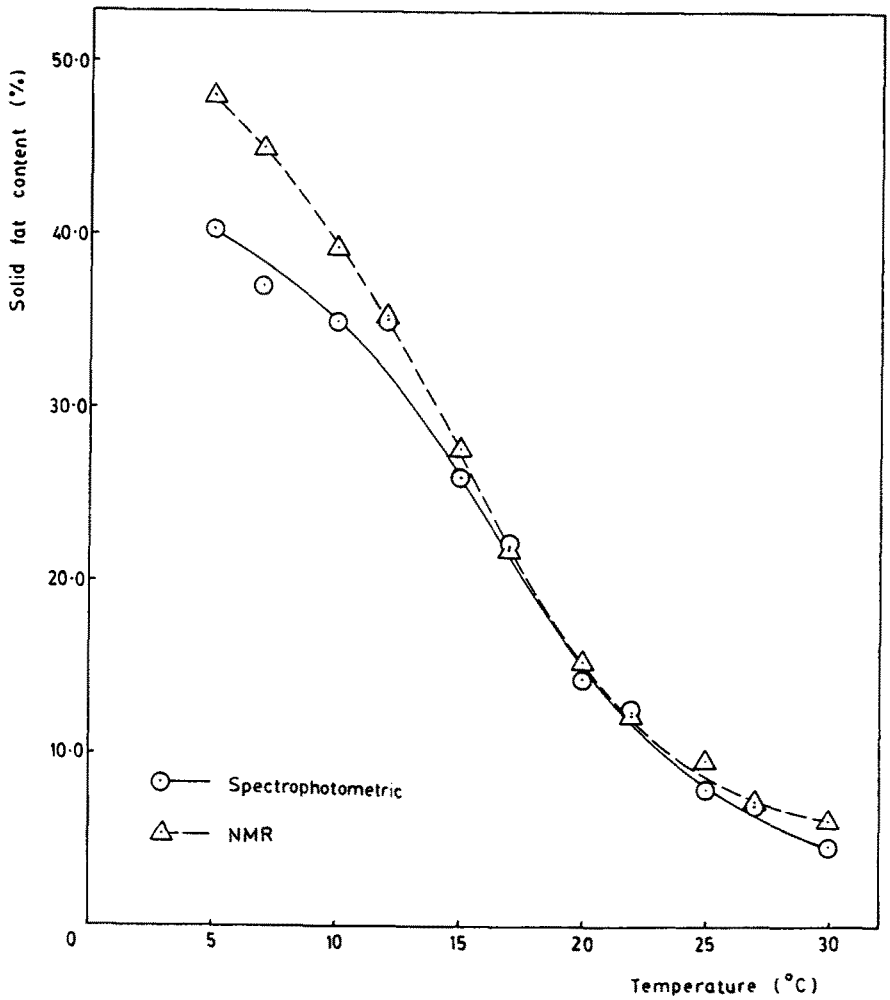

FIG. 1. Solid fat contents of crude palm oil as measured by the centrifugation-spectrophotometric technique and wide-line NMR.

TABLE III

Comparison of Methods for Detection of Stearin Added to Normal Crude Palm Oil

Added stearin (%)	Solid fat content at 30 C (%)		Iodine value[b]
	SP[a] (Y)	NMR (X)	
0	6.65	5.65	54.6
5.2	7.5	7.2	54.2
10.1	8.7	9.7	53.75
15.1	11.5	10.7	52.8
20.1	13.0	12.65	52.1
30.1	15.15	15.35	50.2
40.0	18.2	18.4	48.75
50.0	21.25	20.7	47.1
100	36.0	34.8	39.35
Regression	Y = 1.02 X − 0.06		
Coefficient of correlation	0.998		

[a]Spectrophotometric technique.
[b]AOCS method Cd 1-25.

TABLE IV

Solid Fat Contents of Crude Palm Oil-Stearin Blends Determined at 25 C Using the Tempering Procedure of PORIM (3)

Added stearin (%)	Solid fat content (%)	
	SP[a], Y	NMR, X
0	11.25	11.55
5.2	11.4	13.75
10.1	14.4	15.5
15.1	15.5	16.6
20.1	17.6	18.75
30.1	21.6	22.15
40.0	26.35	26.1
50.0	30.25	29.45
Regression	Y = 1.11 X − 2.80	
Correlation coefficient	0.994	

[a]Spectrophotometric technique.

the fragile dilatometers is not uncommon and replacements may be costly in the long run. In contrast, the spectrophotometric method provides a simple and yet inexpensive means of determining SFC. Analysis requires only the use of a spectrophotometer suitable for measurement around the carotene absorption region and a set-up for good vacuum filtration. Such equipment generally is readily available for other analyses. Indeed, this technique may be used by the palm oil industry for the determination of the solid content of crude palm oil.

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Preliminary Gas Chromatographic Analysis of Flavor Compounds in Mayonnaise[1]

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ABSTRACT

The flavor compounds in fresh, 3- and 6-month-old mayonnaise at room temperature have been analyzed by a gas chromatographic method. The results indicate that as the storage time of mayonnaise increased, the flavor compounds formed from oil in mayonnaise increased. However, the concentrations of allyl isothiocyanate which is the major flavor compound of mustard, and acetic acid and ethyl acetate which are the major compounds in vinegar did not change during the 6 months' storage at room temperature. The analytical method described has shown good reproducibility in the analysis of mayonnaise flavor compounds and can be used as an instrumental analytical method to evaluate the mayonnaise flavor quality and to complement the sensory evaluation of mayonnaise.

INTRODUCTION

Mayonnaise, which is an emulsified, semisolid food, is one of the most common and popular dressings in America. Over 100 million gal of mayonnaise is produced annually in the U.S. (1).

One of the most important quality parameters of mayonnaise is a consistent good flavor. The flavor quality of mayonnaise changes during storage, but little is known about the chemical changes which are responsible for the undesirable flavor change. This paper reports a simple gas chromatographic method which can measure the changes of flavor compounds in mayonnaise during storage.

EXPERIMENTAL

Samples and Sample Preparation for Flavor Analyses

One of the nationwide commercial brands was selected. The 1-oz mayonnaise jars were stored in light at room temperature for 0, 3 and 6 months. After storage the samples were kept in a freezer at -30 C for 24 hr and then thawed in a refrigerator to break the emulsion. The freeze-broken mayonnaise oil portion was then ready for the analysis of flavor compounds.

Preparation and Procedures of Flavor Isolation Apparatus

The apparatus used for the flavor isolation from the oil of emulsion-broken mayonnaise is a modification of the apparatus reported by Jackson and Giacherio (2) and previously described in detail by Min (3) except that the apparatus used here did not contain K_2CO_3 whereas that described by Min (3) did. One mL of oil from emulsion-broken mayonnaise was introduced by syringe on the top of the glass wool in the isolation apparatus, and the flavor compounds were isolated according to the procedures previously described by Min (3). After volatile flavor isolation, the GC column was disconnected from the U-tube apparatus and then connected to the gas chromatograph to separate the isolated compounds in the GC column.

Gas Chromatography

A Hewlett Packard 5880A gas chromatograph with an electronic integrator for gas chromatographic peak area calculation and a flame ionization detector was used.

A 10-ft × 1/8-in. stainless steel column packed with 80/100 mesh Tenax-GC coated with 10% polymetaphenoxylene (Applied Science Laboratories, State College, PA) was used.

The initial temperature was held at 90 C for 2 min and then the temperature was programmed at 4 C/min to 230 C and held at 230 C for 15 min. The nitrogen flow rate was 40 mL/min.

Identification of Compounds

Pentane, acetic acid, ethyl acetate, allyl isothiocyanate and isomers of 2,4-decadienals were identified by comparing the gas chromatographic retention times to those of authentic compounds. These compounds were purchased from Aldrich Chemical Co., Milwaukee, WI.

RESULTS AND DISCUSSION

The flavor compounds in mayonnaise emulsions were first analyzed using the flavor isolation apparatus described by Min (3). The reproducibility of flavor analyses of mayonnaise was not good, which may be due to the combined effects of difficulties of (a) obtaining homogeneous mayonnaise samples for flavor analysis, and (b) accurately transferring 1 mL of mayonnaise sample into the flavor isolation apparatus. Mayonnaise contains a large amount

[1]Ohio Agricultural Research and Development Center Journal Series Article 46-82.