# Determination of the Solid Fat Content of Commercial Fats by Pulsed Nuclear Magnetic Resonance

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## ABSTRACT

A method and instrumentation for measuring the solid fat content is reported that is both accurate and precise. It involves using transient nuclear magnetic resonance (NMR) measurements for determining the percentage of solids in commercial shortenings and hydrogenated oils at selected temperatures. The incorporation of a tempering step at 26.7 C for all samples before measurement has improved the precision of the solids content actually measured (± 0.2% solids) which approximates that of dilatometry. Duplicate measurements are not required to obtain this precision. The instrument is equipped with six 10-mm sample holders in combination with a precise variable temperature accessory system which eliminates the temperature difference between the sample and sample holder. This improved and exact temperature conditioning of samples provides better sample stability and easier handling for routine conditions of analysis. A single temperature result can be made in less than 1 hr and typical 5 temperature results obtained in 2.5 hr. Our work also indicates that tempering does influence results, the net effect being to decrease the amount of solids at temperatures less than the tempering temperature. In comparing the pulsed NMR measured solids with these measured by dilatometry, differences between methods of measurement are minimized when samples have had the same tempering and temperature history. This method provides flexibility, speed, and increased sample throughput of up to 60 samples/day. The self-contained equipment requires only 9 sq ft of space and is ready for measurements within 45 min after start-up.

## INTRODUCTION

The workability and creaming ability of a shortening at any temperature is largely a function of its solid glyceride content at that temperature. For this reason, the solid fat index (SFI) is a good indicator of the plastic range possibilities of a fat or fat blend and has for years provided a means of controlling the consistency of finished products. The SFI test is an empirical measurement of the solids content or quantity of solid glycerides in an oil or fat.

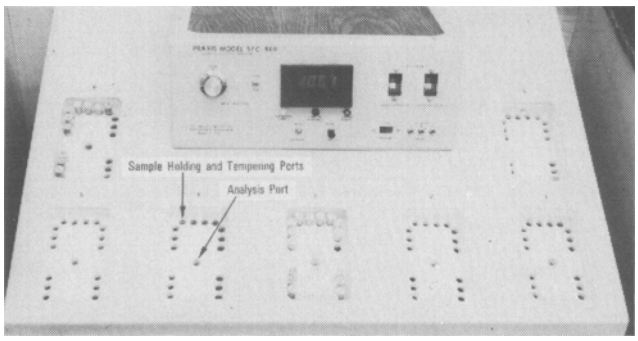


FIG. 1. Praxis SFC 900 Solid Fat Analyzer.

SFI methods used include measurement changes in specific volume (dilatometry), continuous wave proton nuclear magnetic resonance (NMR) (wideline NMR) and the newly emerging nonempirical technique of proton pulsed NMR.

Dilatometry (1-3) is the oldest and widest used method for SFI and is an official AOCS method (4). This method, even though time consuming and applicable only below 50% SFI, is the most precise. The results are not absolute but do have a great deal of comparative value because of the efforts (1,3) to standardize the tempering procedure used to chill and condition the fat in the dilatometery.

The wideline NMR technique (5-12) provided the first attempt at a direct measurement of solids in fats since it depended on the dipole-dipole interactions of rotating glyceride molecules. This approach compares the area under a liquid signal at a given temperature with that of a reference oil. Pohle et al. (7) indicated that the precision of the wideline NMR method decreases with increasing solids level. Swindells and Ferguson (11) found that a dilatometric type of tempering was necessary to eliminate anomalous sample behavior. Reasonable precision, ± 0.5% solids or almost comparable to dilatometry, was obtained by taking the average of three readings and using room temperature to eliminate the changing temperature difference between the sample and sample holder.

Preliminary results obtained by a task group of the NMR subcommittee (12) indicated that solid fat measurements by pulsed NMR might offer precision superior to the wideline NMR procedure. An automated pulsed NMR procedure has been described using the free induction decay (FID) signals (13). Two methods based on this principle were described by Van Putte et al. (14). The first method used a direct ratio of the signal from the solid fat to the signal from the total fat. The second method was an indirect method and measured only the signal from the liquid fat at a time of 70 μsec after applying the Rf pulse. The calculation of solids content uses reference oil data and is similar to the wideline NMR procedure. The indirect method (15) was demonstrated to be the most accurate and achieved a standard deviation of ± 0.28% solids.

A pulsed NMR method based on the use of a standard plot at each testing temperature has been described in an attempt to improve the precision of the method (16). This approach compares favorably with wideline NMR and the indirect pulsed NMR methods but is still less precise than dilatometry.

At the present time there is no standard method for making solid fat measurements by pulsed NMR. Measurements of SFI by an NMR technique are not expected to give absolute % solids values that agree exactly with a dilatometric measurement. This is because of the approximations that are made in dilatometry between the specific volume of the liquid curve and the specific volume at a point on the dilatometer curve at that temperature (1,4).

Recently, relatively inexpensive pulsed NMR instruments have been developed for solid fat measurements. One of these instruments is the Solid Fat Analyzer (SFC 900) from Praxis Corporation. The purpose of this investigation was not only to test this instrument but also to develop a

practical procedure for the solids content determination.

## EXPERIMENTAL PROCEDURES

### Sample Tempering and Conditioning (1)

The samples should be melted completely (at ca. 70 C) and mixed thoroughly. Enough sample is added to a 10 mm OD x 75 mm sample tube so that the meniscus of liquid fat is within 15 mm of the top of the tube and no lower. A tube containing olive oil as the reference standard is prepared in the same manner. Each tube is stoppered and then placed in one of the holding and tempering ports of the 60 C compartment. After 60 C equilibrium is reached in about 20 min, the reference oil is placed in the analysis port, and the NMR reading is measured. After the first measurement of the reference oil, the other samples are measured in sequence and then placed in the 0C compartment and chilled for exactly 5 min. (This compartment has no Analysis Port.) The reference oil and sample are then transferred to the holding and tempering ports in the 26.7 C compartment and tempered for exactly 30 min. For stocks which melt at 26.7 C, a lower temperature is used, i.e., 21.1 C. To determine the percentage of solids at temperatures below 26.7 C, the reference oil and samples are transferred back to the 0 C compartment and rechilled for 5 min. The reference oil and samples are then removed, wiped dry, and placed in the holding and tempering ports of the compartment at the temperature of interest. After 20 min the reference oil is placed in the analysis port and the NMR reading is measured. The other samples are likewise measured in sequence. If measurements are to be taken at a series of temperatures on a given sample, the measurement is taken at the lowest desired temperature first and then at each succeeding higher temperature.

### NMR Measurements

A self-contained pulsed NMR spectrometer (Model SFC-900, Solid Fat Analyzer, The Praxis Corp., San Antonio, TX) having six constant temperature (± 0.04 C) locations for both sample conditioning and measurement was used. Each compartment has 20 ports near the perimeter for holding and tempering samples and a center analysis port where the sample is placed and the NMR reading is measured (Fig. 1). All NMR readings were taken using the following instrument conditions.

| | |
|---|---|
| Magnet strength | 15 Kilogaus |
| Radio frequency | 10.72 MHz |
| Pulse function | 90° |
| Display | Free Induction Decay (FID) |
| Clock | 1 sec |
| Variable delay | 200 μsec |
| Program counter | 8 |
| Mode of operation | Automatic, fast |

The solids content was calculated using the following formula.

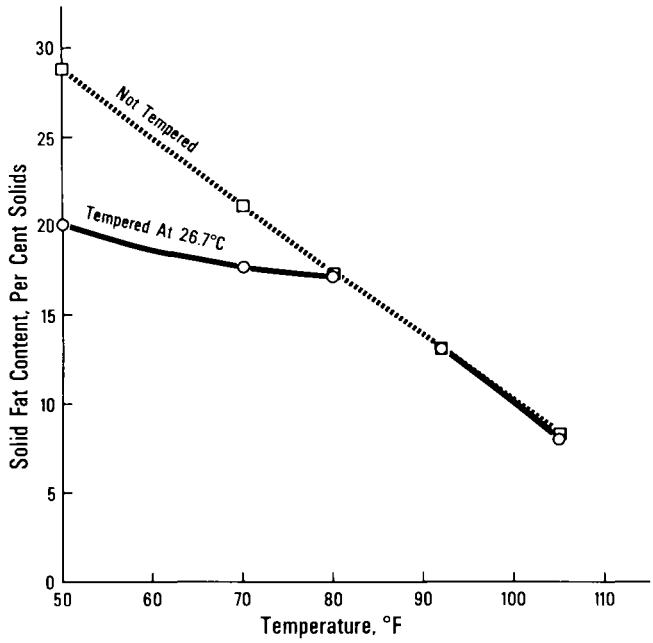


FIG. 2. Effect of tempering on solid fat content.

$$\text{Percent Solids} = 100 - \left[\frac{\left(\frac{\text{sample at T°C}}{\text{sample at 60°C}}\right)}{\left(\frac{\text{reference oil at T°C}}{\text{reference oil at 60°C}}\right)}\right] \times 100$$

Olive oil was used as a reference standard since it remains 100% liquid at all temperatures of interest.

### Dilatometry Measurements

The procedure described by Fulton, Lutton, and Wille (1) was used.

### Consistency

Measurements were made using a Dow Penetrometer and a method based on ASTM D-217-48.

## RESULTS AND DISCUSSION

An experienced analyst can determine the percent solids at five different temperatures on 60 samples in 8 hr. This includes sample preparation, the necessary tempering, and calculating the data.

The tempering period at 26.7 C after solidifying the fat before making the NMR measurement is perhaps the principal difference from present NMR methods. This step was introduced for several reasons. First, the official AOCS dilatometry method (4) includes the same tempering temperature. Second, a major field of interest is the phase behavior of shortenings which are usually tempered for

TABLE I

Solid Fat Content of Commercial Shortenings

| Testing temperatures °C | Solid fat content, percent solids | | | | | |
|---|---|---|---|---|---|---|
| | Sample 1 | | Sample 2 | | Sample 3 | |
| | Pulsed NMR | Dilatometry | Pulsed NMR | Dilatometry | Pulsed NMR | Dilatometry |
| 10.0 | 21.65 | 20.27 | 26.53 | 24.57 | 14.56 | 13.78 |
| 21.1 | 16.71 | 16.62 | 17.73 | 17.63 | 11.58 | 11.13 |
| 26.7 | 15.88 | 15.80 | 16.59 | 16.47 | 10.32 | 10.98 |
| 33.3 | 12.25 | 12.42 | 12.96 | 12.89 | 9.60 | 9.68 |
| 40.6 | 6.77 | 6.90 | 6.96 | 7.08 | 5.12 | 5.62 |
| Average $\sigma$ | 0.20 | 0.16 | | | | |

TABLE II

Solid Fat Content of Commercial Shortening Bases and Conventional Hardstocks

| Shortening bases | | | Conventional hardstocks | | |
|---|---|---|---|---|---|
| Solid fat content, % solids, 10.0 C | | | Solid fat content, % solids, 21.1 C | | |
| Sample | Pulsed NMR | Dilatometry | Sample | Pulsed NMR | Dilatometry |
| 1 | 1.59 | 1.89 | 1 | 75.1 | 72.4 |
| 2 | 3.04 | 3.00 | 2 | 40.9 | 36.9 |
| 3 | 4.71 | 5.20 | Avg. $\sigma$ | 0.41 | 0.34 |
| 4 | 2.91 | 2.80 | n = 2 | | |
| 5 | 3.40 | 3.80 | | | |
| Avg. $\sigma$ | 0.38 | 0.34 | | | |
| n = 3 | | | | | |

TABLE III

Solid Fat Content of Commercial Shortenings Determined by the Standard and Rapid Pulsed NMR Procedures

| | Solid fat content, percent solids | | | |
|---|---|---|---|---|
| Testing temperature, °C | Sample A Standard method | Rapid method | Sample B Standard method | Rapid method |
| 10 | 22.20 | 22.49 | 26.53 | 25.86 |
| 21.1 | 17.11 | 16.83 | 17.73 | 17.30 |
| 26.7 | 16.03 | 15.91 | 16.59 | 16.67 |
| 33.3 | 11.68 | 11.78 | 11.96 | 11.57 |
| 40.6 | 6.94 | 6.63 | 6.96 | 6.56 |
| Avg. $\sigma$ | 0.20 | 0.22 | 0.20 | 0.24 |
| Time required, min | 150 | 45 | 150 | 45 |

TABLE IV

Precision of Solid Fat Content Methods

| Method | Standard deviation of method, % |
|---|---|
| Dilatometry (1) | 0.2 |
| Wideline NMR (11) | 0.5 |
| Pulsed NMR indirect method (15) | 0.28 |
| Pulsed NMR standard plot (16) | 1.0 |
| Standard pulsed NMR (this work) | 0.20 |
| Rapid pulsed NMR (this work) | 0.23 |

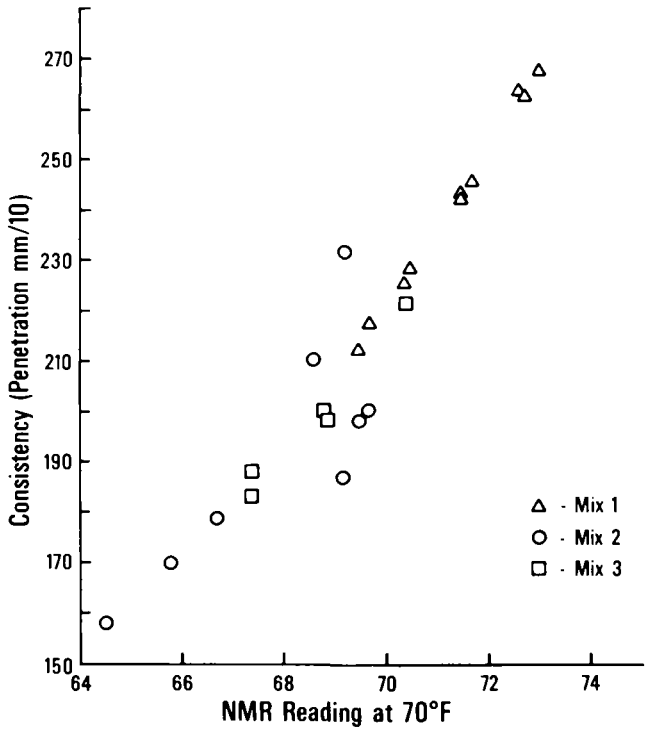


FIG. 3. Relationship between consistency at 70 F and NMR measurements.

some hours at a temperature near 26.7 C after being packed. Third, it was demonstrated experimentally that sample equilibrium was reached much more rapidly and reproducibly when the 26.7 C tempering step was included in the method. Without tempering, the NMR reading tended to drift before an approximate steady state was established. The same findings were reported by Filton, et al. (1). Fourth, in order to compare solid fat content results between pulsed NMR and dilatometry or between labs, it is essential that test samples also have the same temperature history. This is a characteristic of the sample not of the measuring technique and cannot be avoided or overlooked if precise, high quality results are to be obtained.

Figure 2 shows the effect of 26.7 C tempering on the percent solids-temperature relationship of a commercial shortening. The effect of tempering is to decrease the amount of solids at temperatures less than the tempering temperature. This leads to more accurate determination of the content of intermediate melting and trisaturated glycerides.

Three commercial shortenings with a range of solids content were analyzed in duplicate using this pulsed NMR procedure on different days by the same analyst. These same samples were also analyzed using dilatometry. The results by the two different methods (Table I) agree exceptionally well at those temperatures above the tempering temperature of 26.7 C. The NMR results are higher than dilatometry at 10 C, and this difference is attributed to the approximations made in the SFI calculation by dilatometry. The data were examined statistically, and the overall standard deviation was attained by a single NMR measurement is ± 0.2% solids. The reproducibility within a day, between days, across samples and days showed no significant differences. It was concluded that the NMR reproducibility successfully approximates that of dilatometry.

Table II lists the solid fat content results for commercial shortening bases (10.0 C) and conventional hardstocks (21.1 C) obtained by pulsed NMR and dilatometry. The results by the two methods have comparable precision, and NMR results at the higher solids level are again higher.

Our data support prior conclusions (7,9) that no overall

correlation for all samples and all temperatures (especially at low temperatures and high solids) can be made between NMR results and SFI results. However, a pattern is indicated that for specific type samples (i.e., commercial shortening bases and hardstocks), the NMR and SFI dilatometry results obtained from having the same temperature history are comparable. This should provide a means of developing acceptable agreement and understanding of differences, when encountered.

It is possible to further reduce the elapsed time for measurement of solids content. This is accomplished using a multiple sampling approach. Five separate tubes of a given sample are filled and with the reference oil tempered as previously described. A single tube is then placed in one of the holding and tempering ports of the respective compartment at each of the five temperatures of interest. After 20 min, the pulsed NMR reading of each tube is measured. The results of this rapid multiple sampling method for two commercial shortenings are shown in Table III. The elapsed time can be reduced from 2.5 hr to 45 min, with no apparent loss in precision or accuracy.

The precision of various methods for measuring the solids content are compared in Table IV. Both methods described in this work compare favorably with dilatometry.

Since the separate sample compartments of the SFC-900 Solid Fat Analyzer have their own individual temperature control system, it is possible to extend the measurements of solids to lower temperatures. We have successfully measured solids at 0 C on products like winterized oils.

Consistency is usually measured by micropenetrations and plotted vs. the solids content. This relationship is used in the blending of glycerides so that the product will remain workable within desired temperature ranges. Again the accurate measurement of micropenetration also depends upon the temperature history of the sample. Given the same temperature history, PNMR readings can be used to predict micropenetration.

A series of commercial shortenings for which micropenetration values had been determined were given the same temperature history, and the PNMR reading of each sample was measured. Figure 3 shows a plot of micropenetration vs. the PNMR reading of each sample. Good correlation between the finished product consistency (micropenetration) and the PNMR reading is demonstrated for mixes 1 and 3. Samples of mix 2 which contained high levels of polymorphic fat show a high scatter between PNMR readings 68-70. This suggests that these conditions of tempering and/or type of measurement do not extend to all fat compositions. The samples were subsequently analyzed on three different days. A statistical treatment of the data showed that the standard deviation of the PNMR measurement is ± 0.3 reading units and this corresponds to a predicted micropenetration value of ± 4 units. This approach of measurement and prediction of micropenetration is rapid enough to be used for control purposes at certain points in the process.

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