Standardization of Nuclear Magnetic Resonance Measurement of Solids in Fats and Shortenings

W. D. POHLE and R. L. GREGORY, Swift and Company, Research and Development Center, Chicago, Illinois

Abstract

An investigation of factors that influence the measurement of solids in fats and shortenings by nuclear magnetic resonance was directed toward standardization of the method. The aim was to select abbreviated tempering conditions that would yield results comparable with those existing at temperature equilibrium. Conditions were found which reduced the time and gave an accuracy that made the method suitable for both research and control purposes.

Introduction

REPORTS ON THE APPLICATION of nuclear magnetic resonance (NMR) measurements to the determination of solids in fats and shortenings (1–4), have been concerned primarily with showing the solids content of samples at selected temperatures and pointing out the superiority of these measurements over other techniques for evaluating solids content. Although investigators have standardized the testing for their own purposes, little or no information is available on the factors necessary for obtaining comparable results in different laboratories. These factors involve instrument calibration, appropriate chilling temperature and time, and tempering time that will give results comparable with equilibrium conditioning in as short a time as possible. This report will deal with the effect of these various factors on the determination of solids and selection of the conditions which, in a minimum time, give results identical with or close to the equilibrium values.

Measurement by Nuclear Magnetic Resonance

For this purpose a low resolution NMR instrument, Schlumberger NMR Analyzer Model 104,[1] was employed. The first step in the application of an instrument of this type is the establishing of appropriate settings for the various parameters, based upon characteristics of the material to be tested and upon the size of sample to be employed. The conditions employed for the reported data were:

Sample size	4.5 to 5.5 grams
Instrument settings	
Sweep time	1 minute
Sweep constant	1 second
R.F. selector	40 df
Sweep amplitude selector	0.5 gauss
Sensitivity selector	X 500
Modulation amplitude selector	0.1 gauss
Integrator settings	
Read-out multiplier	2
Threshold, mv	0.1
Signal multiplier	5

In preparing a sample for testing, a procedure must be followed which is reproducible. The principal steps are heating the sample to a selected starting temperature, chilling to a point where the solids formed are greater than they will be at the testing temperature, and tempering in a bath with proper temperature control for a period that will give equilibrium or conditions close to those existing at equilibrium.

After appropriate instrument settings and a satisfactory procedure for preparing the sample have been established, the next step is calibration of the instrument.

Instrument Calibration

A calibration curve can be established from a sufficient number of measurements on a series of liquid oils, which will give a reliable average value for the liquid oils, at the desired testing temperature. The calibration curve for the selected temperature is prepared by plotting the average of the series of measurements on the liquid oil as 0% (zero) solids and zero NMR measurement as 100% solids and then drawing a straight line between the two points. Measurements on a solid fat are not necessary as a completely solid fat will measure zero. Samples of vegetable oil hydrogenated to a low iodine value may measure 0 to 1 mv/g at room temperature but, on cooling, will measure zero, indicating the presence of a small amount of liquid at room temperature.

Measurements made on a series of oils at 0, 28, and 60C indicated that soybean, cottonseed, and peanut oil were similar and that safflower oil gave slightly lower NMR values, also that these values vary with temperature. Typical measurements are given in Table I. Thus, in preparing calibration curves, one must take into account both the testing temperature and the type of oil. Since soybean and cottonseed oils are the most typical oils processed, the calibration curves for different temperatures given in Figure 1 are based on the average values for these oils over the range of 0 to 60C. Values below 0C are taken from an extrapolation of the data to −15C. This extrapolation is in line with data for safflower oil, which were carried to −10C without solids appearing in the sample, as evidenced by the NMR measurements and the visual clarity of the sample.

In the past it has been the practice to set up calibration curves which were based on measurements made of known blends of completely hydrogenated oils with liquid oil. These have followed a straight line connecting the NMR value for the liquid oil (0% solids) and zero NMR value (100% solids), within the limits of the method, when the measurements were made in the region (0 to 30C), where the hydrogenated oil has not gone into solution appreciably.

TABLE I

Typical N-M-R Measurements on Liquid Vegetable Oils

Temperature	Safflower oil	Soybean oil	Cottonseed oil	Peanut oil
0C	65.2	65.5	64.6	64.5
28C	60.7	61.5	62.2	61.6
60C	56.5	57.6	57.4	57.6

[1] This model has been replaced by Varian Associates as Model PA-7 Process Analyzer.

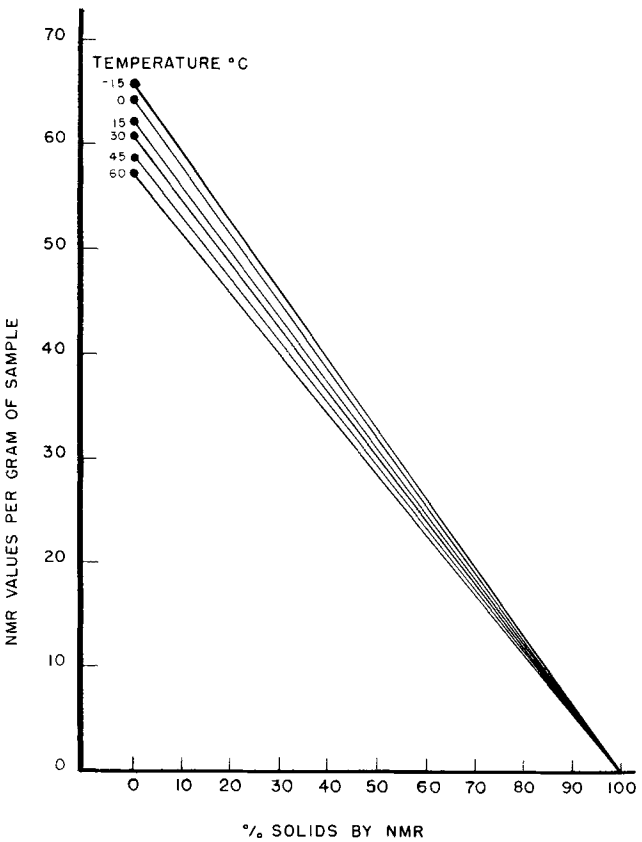

FIG. 1. Calibration graphs showing the effect of temperature.

This new approach to the preparation of a calibration graph saves time and increases the accuracy of the measurement of solids at a selected temperature.

Chilling and Tempering

In previous reports by the authors, samples were chilled at 0C and for a time were comparable with that used in the Solids Fat Index (SFI) method (3) because subsequent measurements were going to be compared with SFI data. Subsequent work has revealed that chilling at 0C for the short periods selected was not adequate to solidify all the material that would be solid at 10C. This was evidenced by the increase in solid content of certain samples with time, when held in the 10C bath after chilling at 0C.

To attain results in a short time which will be comparable with those at equilibrium, it is necessary to approach the equilbrium conditions from the solid side. To accomplish this the sample must be chilled to a point where more solids are formed than will be present at the tempering temperature. If chilling is to be done rapidly, so that the method is suitable for routine testing, a very low temperature bath must be used. A carbon dioxide-acetone bath maintained at below −60C was the simplest and most convenient means for chilling the samples. Samples heated to 70C and placed in the carbon dioxide-acetone bath were chilled to −30C in 10 min. At −30C all of the glycerides solid at 0C and some or most triglyceride liquid at 0C will be in the solid state. Samples chilled as low as −40C attained the temperature of the tempering bath in 15 min as measured by a thermocouple in the center of the sample. This provided conditions satisfactory for obtaining an excess of solids prior to tempering. The temperature attained in the sample during tempering appeared to offer conditions that would be close to equilibrium after 30 min of tempering.

Tests made to show the effect of 5-, 10-, and 15-min chilling in the −60C bath, followed by tempering at 10C for 20, 30, and 50 min and for 16 hr, are shown graphically in Figure 2 for a lard and a tallow. Previous tests on these two fats after chilling at 0C had indicated inadequate chilling. The results in Figure 2 indicate that 10 min of chilling in the −60C bath, followed by 30 min of tempering, would probably be satisfactory for routine testing and give results comparable with those at equilbrium (16 hr of tempering).

Measurement Tempered at 10 to 37.8C

In routine tests at a variety of temperatures the instrument will be maintained at a constant room temperature. If the samples are colder than room temperature, melting of the solids will occur with time. If the samples are warmer than room temperature, solids will form with time. Under these conditions it may be appropriate to deviate from the normal practice of taking the average of the first two sweep measurements. The operating procedure that will give the best results, based on tests made on 15 shortenings and five hydrogenated vegetable oils in which the samples were heated to 70C, chilled 10 min in the −60C bath, then measured after 30 min and 16 hr of tempering, are summarized in Table II. All measurements were based on the average of the first and second sweep except when indicated otherwise.

Under the conditions illustrated in Table II the precision of the method, as expressed by the standard

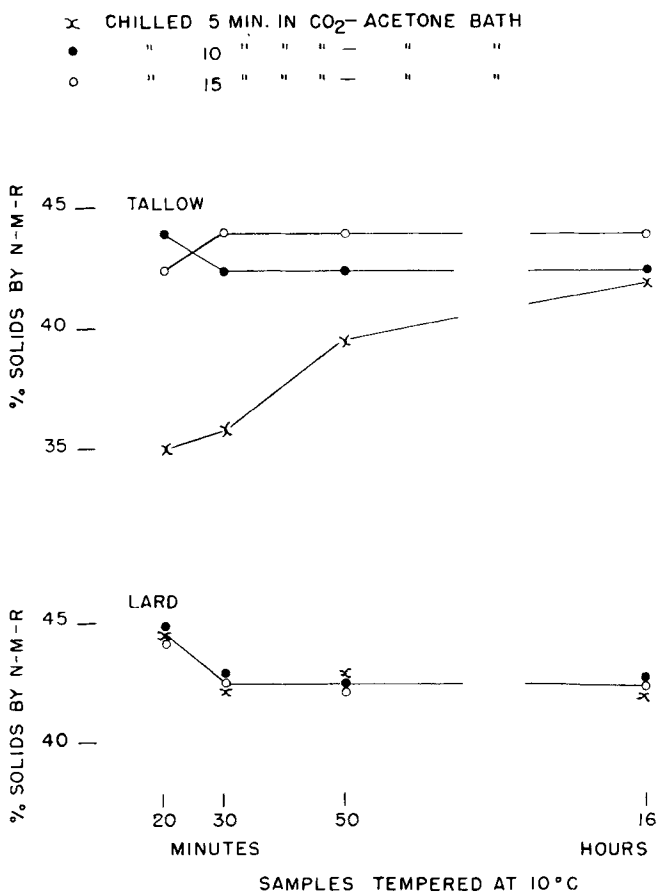

FIG. 2. Effect of chilling and tempering time on solids found when tempered at 10C.

TABLE II

Summary of Data for the Determination of Solids in 15 Shortenings and Five Hydrogenated Vegetable Oils after 30 Minutes and 16 Hours of Tempering

	Tempering Temperature, °C				
	10	21.1	26.7	33.3	37.8
Tempered 30 minutes	50.3[a]	32.4	23.7	11.2	10.2
Tempered 16 hours	50.4	31.1	22.6	11.2	9.2

[a] Average of the second and third sweep used for calculating the solids content.

deviation, is approximately ±1.0%, and the 95% confidence limits for a single value (average of two sweeps) is approximately ±2.0%.

The precision of the method and accuracy of the results obtained after 30 min of tempering are satisfactory for routine analysis, control analysis, and many research studies. Greater accuracy can be attained as required, by appropriate changes in chilling, tempering, and/or increasing the number of determinations on the same sample.

The conditions reported in this paper covering instrument calibration, chilling, tempering, and measurements have simplified the preparation of a calibration graph without sacrificing accuracy and reduced the time required for a test to a minimum while at the same time retaining accuracy. The testing parameters set forth should make it possible to obtain comparable results in different laboratories which would be only slightly more variable than those within a laboratory, for example, than those reported in this paper.

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