# A New Wide-Line NMR Analyzer and Its Use in Determining the Solid-Liquid Ratio in Fat Samples[1]

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## ABSTRACT

A new, simple, inexpensive wide line NMR analyzer is commercially available and suitable for several applications in the oils and fats industry. Its use to determine the solid-liquid ratio in fats has been studied in particular, and it has been found that the solids content of a fat can be determined at four temperatures in approximately one hour. The reproducibility of the measurements is 1% absolute solids. The results obtained are compared with those obtained by dilatometry on the same samples. Several different methods of calculation and operation were tried; differences in the results are given. Arguments for and against four particular methods of calibration are discussed.

## INTRODUCTION

Many previous workers have studied the possibilities of replacing existing dilatometric procedures with wide line NMR measurements for determining the solid-liquid ratio in fat blends (1-3). Their findings all showed that wide line NMR had much to offer the analyst regarding speed and ease of operation. It also provided a means of directly obtaining the liquid content of a fat, which is not the case with SFI values, and for the "as received" condition of blends without melting the sample first.

The progress of the new method from a research project to a regular quality control tool was hindered by the relatively high expense and the complexity of the apparatus. New types of wide line NMR spectrometers are now available which are relatively inexpensive, simple to operate and which perform reliably in industrial environments. This paper will describe one such spectrometer and some of the results obtained with it in the determination of the solids content of fat blends.

The Newport NMR Analyzer is a wide line spectrometer using a permanent magnet with a field strength of 640 gauss. The overall dimensions of the magnet case are 17 x 11 x 7½ in. and it weighs 133 lb. The dimensions of the electronics console are 21 x 17 x 16¼ in. and this weighs 95 lb. Two sizes of sample can be used, either 2 ml, containing approximately 1.7 g of fat (this is the size used for all the work mentioned here), or 40 ml, containing 35 g of fat. The two sample assemblies are easily interchangeable, both using the same magnet. The magnitude of the NMR signal is read off a panel meter or from a digital voltmeter.

The phenomenon of NMR is achieved by placing the sample inside the radio-frequency (r-f) coil at the center of the volume of homogenous field inside the permanent magnet. A triangular waveform current passing through the modulation coils on the magnet sweeps the field through 3.5 gauss peak-to-peak, with a frequency of about 32 Hz. The NMR absorption is produced each time the field is swept through the gyromagnetic resonance value corresto the frequency of the r-f oscillations which are at approximately 2.7 MHz. By adjusting the r-f oscillator two resonances can be produced every cycle, and hence about 60-64 resonances are produced per second. The energy absorbed from the r-f coil by these resonances produces a characteristic modulation of the r-f envelope. This modulation is detected and amplified in a stable gain, a.c. coupled amplifier.

The resonances from protons in the liquid and solid states are separated by means of restoring gates which are opened only long enough to permit the passage of the narrow band liquid resonances. Thus the area under the chain of pulses from the sample is proportional only to the number of protons in the liquid state. An output at the rear of the instrument provides a continuous voltage that is proportional to the magnitude of the signal for continuous recording purposes. The pulses are fed to an integrator which integrates for a fixed period of time, either 8.2, 33.0 or 132 sec. At the end of the integration period, the integrated voltage is displayed. The precision of the measurement increases in the ratio of 1:2:4 with increasing integration time. The system can also be used with a printout facility.

The instrument incorporates a low noise oscillator circuit that provides a stable r-f level which is adjustable from about 30 $\mu$A up to 500 $\mu$A. It has an automatic loss control which compensates for any variation in dielectric or conductive losses from sample to sample.

The unit has found many industrial applications, e.g., determining the amount of moisutre in grain, starch, tobacco, wood chips, rayon, coal, of solvents in plastics, of the water content of mineral ore slurries, detergent slurries, sewage, and of the oil content of seeds, leisure foods and yarns. It is also used extensively for replacing dilatometric procedures in determining the solid-liquid ratio in fats.

In order to obtain the best possible results with any materials in the unit, the optimum r-f level for that material has to be determined by experiment. This is usually a compromise between choosing as high a value as possible in order to obtain a good signal noise ratio, and restricting the amount of r-f saturation occurring. Saturation curves were drawn for five different soft oils and two fat blends and from these curves 60 $\mu$A was chosen as the most suitable level to employ when using 2 ml samples. Supplementary modulation was also employed in order to minimize the effects of slight r-f saturation. This reduces the instability of the readout associated with a saturating sample and it recovers some of the signal lost because of saturation.

Next, the temperature dependence of the NMR signal was investigated for several soft oils. Samples of each type of oil were equilibrated at various temperatures covering the range 20 to 60 C. The NMR signal from them was measured in the Quantity Analyzer fitted with a sample temperature controller to prevent the samples from changing temperature during measurement. Figure 1 shows the results for three of the oils. All the samples, however, produce the same slope, which is somewhat greater than expected theoretically. This may be due to increasing r-f saturation at any particular r-f level, as the viscosities of the samples fall with increasing temperature. Thus if the NMR method chosen involves measurement of the signal from a blend at a temperature where it is completely molten, then it is not correct to apply the simple 1/T law to determine the signal from the liquid phase of the blend at any other temperature.

Although it is wrong to assume that the actual liquid

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[1] One of 10 papers to be published from the Symposium "Wide Line Nuclear Magnetic Resonance" presented at the AOCS Meeting, Minneapolis, October 1969.

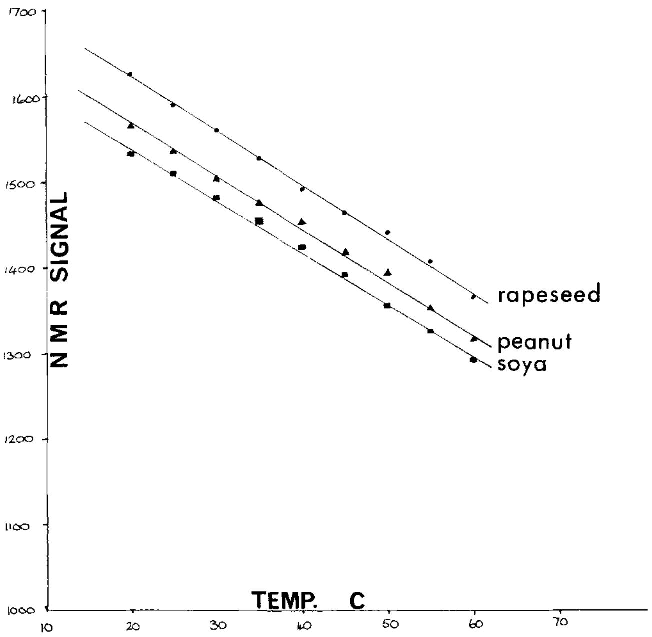

FIG. 1. Dependence of NMR signal from fats and oils on temperature.

phase has the same composition through the entire melting range of a blend, the total hydrogen content does not alter significantly to make it an important source of error in the values for the solids contents calculated. Thus by equilibrating five weighed samples of a blend, one at each of the four temperatures at which one wishes to measure the solids content and one at a temperature where it is completely molten, and by applying the correct temperature correction to the signal from the completely molten sample, the solids content of the blend at each temperature may be calculated by comparison of the actual measured NMR signal from the blend with that calculated for a 100% liquid sample at the same temperature. The result will not necessarily be in close agreement with the SFI value for the blend at that temperature.

Another method by which the solid-liquid fat ratio can be determined is by comparing the signal from the blend conditioned at the correct temperature with that from a soft liquid oil at the same temperature, thus:

$$\text{Percentage solids at t C} =$$

$$100 - \frac{\text{NMR signal per gram of blend at t C}}{\text{NMR signal per gram of liquid oil at t C}} \times 100$$

Three points should be remembered if this method is adopted. First, the signal from one type of soft oil is different from that from another and this variation can cause changes in the apparent solids content of a blend. The apparent percentage solids in a blend at 19 C when the signal from it is compared with that from various soft oils at 19 C is equal to 41.5% using a peanut oil calibrant, 37.4% using soybean oil, 43.0% using rapeseed oil and 41.5% using cottonseed oil. Second, the signal from various samples of soft oils can vary with changes in the total hydrogen content of the oil because of different fatty acid compositions. Variations of 0.49% for rapeseed, 0.83% for soybean and 1.09% for peanut oil have been recorded. Third, changes in composition of the blend are not taken into account.

The first two points could be eliminated by acceptance of a primary standard such as triolein for interlaboratory agreement. Figure 2 is typical of results using this method; NMR indicates a higher solids at low temperatures and a lower solids at high temperatures. Calibration graphs between NMR and SFI results can be made, though a different curve is required at each temperature of interest. From approximately 40 blends tested, only two or three did not lie on a common curve at each temperature.

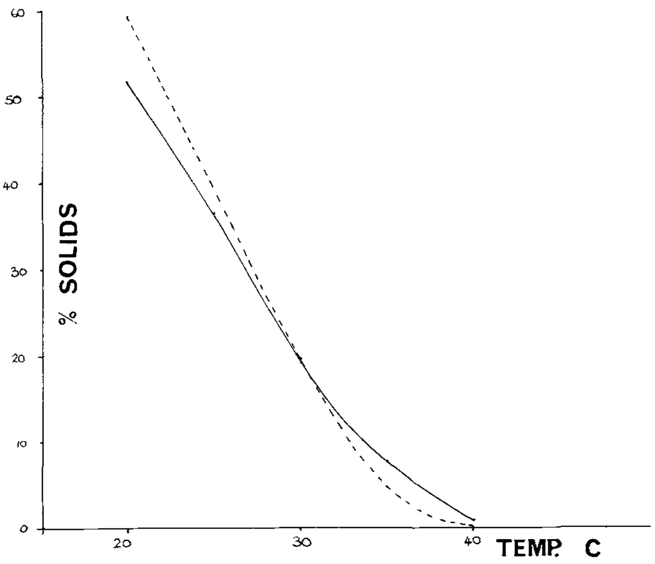

FIG. 2. Comparison of NMR results using a soft oil calibrant to dilatometric results. ——, Dilatometric curve; - - -, NMR.

A third method of using the NMR Analyzer to control the quality of fat blends is to use, as calibrant, a sample of blend whose SFI values at each temperature have been determined by dilatometry. In this method, the unknown samples are conditioned along with a sample of the known blend, and after equilibration the signals from the unknowns are compared with that from the known sample. A simple proportional calculation gives the SFI values of the unknowns at that temperature, but it must be remembered that the NMR signals are a measure of the liquid contents of the blends and not the solid contents.

If the blends that are being compared are similar in composition with regard to their basic oils, then agreement in results between SFI values calculated by NMR and actual SFI values measured by dilatations are very good. Figure 3 shows this good relationship for one particular blend. If the two blends being compared are very different then correlation is poor. The results obtained by this method are SFI values and hence are not an actual measure of the solids content of the blend, but results are obtained in 50 to 60 min.

Many different equilibration procedures were tried in

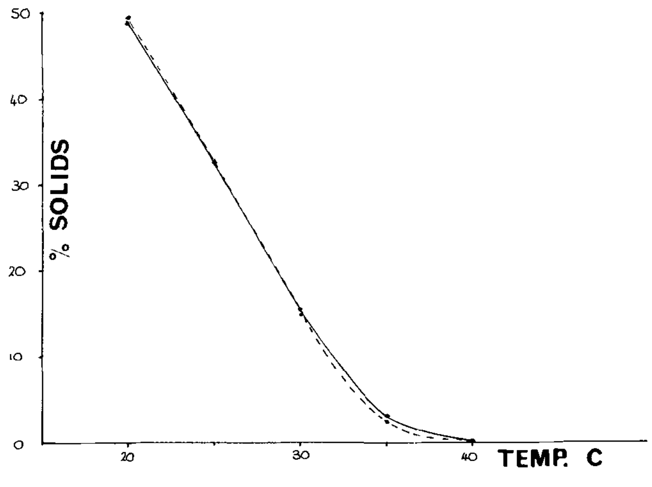

FIG. 3. Comparison of NMR results using a calibrant blend to those obtained by dilatometry. ——, Dilatometry; - - - NMR.

TABLE I

Reproducibilities Obtained (%)[a]
With Various Fats at Four Temperatures
After Equilibrating for 20 Min in Ice
and 20 Min at Temperature

| Sample | 20 C | 30 C | 37 C | 42 C |
|---|---|---|---|---|
| Blend A (hard) | 0.4 | 0.4 | 1.0 | 0.6 |
| Blend B (soft) | 0.5 | 0.5 | 0.9 | 1.0 |
| Blend C (very soft) | 0.4 | 0.6 | 0.9 | 0.8 |
| Hardened fish oil | 0.5 | --- | --- | --- |
| Palm oil | 0.6 | --- | --- | --- |

[a] The figures quoted show the variation in the solids content determined in this manner on 20 analyses, e.g., the variation in solids content of blend A at 30 C was found to 0.4% absolute.

order to determine the shortest time that was required to obtain a signal that was reproducible to within 1.0% at all temperatures. Three different blends were tested, together with a sample of palm oil and one of hardened fish oil. Procedures varying from 1 hr in dry ice and 1 hr at the chosen temperature, to 10 min in ice and 20 min at temperature were tested. From the results of this work the following procedure was adopted: 1.7 g of completely molten blend contained in a 2 ml sample tube were placed in an ice water bath for 20 min, and then in an aluminum block, which was maintained in a water bath at the appropriate temperature for 20 min. At the end of this time the NMR signal was measured.

Table I gives the reproducibility of the solids content calculated from the NMR signals for the five samples after conditioning at four temperatures in this way.

Twenty duplicates were done for each value quoted. From a thermocouple buried at the centre of one sample it was found that the blend reaches OC, 7.5 min after insertion in the ice bath, and 20 C after 9 min in the alumininum block.

After so short an equilibration time it was thought that the sample might be far from true equilibrium. Thus eight samples were conditioned in this way and their NMR signals were determined every half hour for 30 hr. The greatest change in solids content observed in this time was 7.6% for palm oil, next was 4.6% for hardened fish oil and the least was 1.5% for hardened palm kernel oil. Since any analyst would follow a control procedure fairly closely every day, then, although some samples might not quite be at equilibrium, the results would be reproducible and would enable good control of the product.

When the samples had been conditioned in the aluminum blocks they were transferred to the sample assembly of the analyzer which was at room temperature. Thus the sample temperature was changing continuously during measurement. The rate was of the order of 4 C/min initially, thus the measurement of the NMR signal was done by taking the mean of two, 8.2 sec integrations. This required the sample to be in the sample holder for a total of 36 sec. As the sample cooled the wide line NMR signal increased at a rate which was the result of two opposing effects: as the temperature decreased, the liquid phase tended to solidify, so reducing the magnitude of the signal; and the signal per unit weight of liquid increased as the temperature decreased. Thus these two effects tended to oppose one another and the signal magnitude increased only slowly.

The signals from several samples of different types of blends were plotted with respect to time and in all cases the extrapolated slope cut the 0 min axis at a point less than 1% away from the mean of the first two integrations. As the value of the signal at 0 min would be the value of the signal from the sample in the block, the errors introduced because of the lack of temperature control were small. However, the further the temperatures of measurement are away from ambient, then the greater are the errors introduced; accordingly for reproducibilities greater than 1.0% and for the best possible accuracy, a sample temperature controller should be used.

## DISCUSSION

Many previous workers have shown that wide line NMR provides a convenient,rapid and very accurate method of determining the solid-liquid ratio in a fat blend. This paper has tried to describe the general methods that can be used for this technique, and to elucidate some of the problems that require attention. It has also shown that less expensive types of equipment can be used to obtain good results with a minimal amount of operator skill and knowledge. Hence wide line NMR is a good alternative to the slow, laborious dilatometric techniques.

### ACKNOWLEDGMENTS

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