Application of Wide-Line NMR to Analysis of Cereal Products and Fats and Oils[1]

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Abstract

The principal areas of interest to cereal and oil chemists of wide-line NMR have been reviewed. It provides a rapid method for moisture in cereals where a large number of analyses are required. In the field of plant breeding and genetics of oil seed it provides a non-destructive means of selecting seeds for test and evaluating the seeds grown. In the area of fats, oils and shortenings it provides a rapid and accurate means of measuring the solids content over a wide range of temperatures and can be applied to a finished product as is, under selected conditions.

Introduction

WIDE-LINE NUCLEAR magnetic resonance (NMR) has been used almost exclusively for quantitative analysis while high resolution NMR has been employed for elucidation of molecular structure and motion. This is because wide-line NMR instrumentation and techniques are simpler, meet the requirements for quantitative analysis and are more readily adapted to quantitative analysis under laboratory conditions.

In the area of cereals and fats and oils wide-line NMR measurements have been applied successfully to the determination of moisture in carbohydrate materials (6), fat in seeds (7), and the solid and liquid portion in fats and shortenings (9,11,14). Before taking up the applications and results we will review briefly some of the basic principles of NMR. Details concerning the theory and factors involved in NMR measurements can best be obtained from books and publications (2,8,13) in this area. The references given are intended as a starting point and in no way represent coverage of the field.

Wide-line NMR is a term used to describe low resolution nuclear magnetic resonance. This technique is applicable in studies where differentiation based on gross chemical nature or physical state is desired. For example in studies involving the proton (hydrogen nuclei) it is possible to separate instrument signals coming from the hydrogen in water and hydrogen in solid materials based on line widths. It is also possible to differentiate signals in a fatty system based on solid vs. liquid state.

High resolution on the other hand permits an exacting examination of relatively pure compounds with regard to specific structure and location of structures in the molecule.

High resolution NMR is a powerful research tool while low resolution (wide-line NMR) has found application in many process control situations.

Procedures and Data

Determination of Moisture

In the middle fifties Shaw and Elsken reported on the determination of moisture by wide-line NMR in aqueous suspensions of starch (15) and dehydrated potatoes (14) and Conway et al. (6) on its application to a variety of products such as starch, corn syrup, jelly bean centers and fondants. Since then Varian Associates (17) have presented data and graphs for application to a wide variety of products that include, rolled oats, dextrin, paper board, paper pulp, grated cheese, silica gel, tea and other products. These applications are based on their work and that of the Schlumberger Well Survey Corp., the developer of the wide-line NMR for control purposes.

The first application to production control was at Corn Products Co. approximately 10 years ago based upon the work of T. F. Conway. Since then it has been applied in the cereal and tobacco industries where high volume moisture analyses are required on carbohydrate materials.

An instrument is capable of handling approximately 45 to 80 samples an hour depending on the sweep time per sample. Whether 60 or 30 seconds. However, the number of analyses a single operator can complete in an hour will depend upon the time spent on, preparing and weighing the sample, testing, calculating and cleaning of equipment. If only weighing, testing and calculating are involved a test can usually be completed in 2 to 3 min and a single analyst may complete 20 to 30 analyses per hour. Thus this procedure provides a minimum of operator time and the potential for high volume moisture analyses.

Application of wide-line NMR to the determination of moisture is not simply a matter of purchasing an instrument, placing a sample in the cell, throwing the switch and reading the moisture content. Before this can be accomplished a calibration graph or table must be prepared for the product to be analyzed. This involves, first, the selection of an appropriate sample preparation, sample size, loading of the test cell and selecting settings for the instrument so that all moisture levels from the lowest and highest values can be measured with appropriate distinction. Then a series of samples covering the range are measured and the instrument readings are compared with the moisture content determined by an official or accepted method.

NMR measurements may be applied to any moisture levels but usually have been used in the region of 2–20%. The sample size and instrument settings are selected to obtain a miximum response between the sample with the lowest and highest moisture content. For example, applied to immature, mature and air dried corn the range would be 10–50%; to whole mature corn 10–22%; to a high moisture starch 18–24%; and to a lower moisture starch it may be 7–11% or 4–7%. A single calibration graph may apply over an extended range for several products, or a separate curve may have to be made for each product due to composition, processing or other factors. Examples of calibration curves and applications are to be found in Application Notes by Varian Associates (17).

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Determination of Oil in Seeds

The determination of oil in seeds may be accomplished by measurement on seed dried to less than 5% moisture or measuring the oil extracted into carbon tetrachloride. Carbon tetrachloride was chosen as a solvent because it contains no hydrogen and thus only the oil extracted is measured in the solvent. In 1963 Conway et al. (7) presented data on the determination of oil in seeds from 18 plants, including corn, soybean, castor, linseed and tung seed. The oil content varied from 2% to 50%. The correlation coefficient was 0.993 and if the NMR readings were adjusted for the hydrogen content of the oil the correlation coefficient was 0.999. The time required for a given test was reported as 3 min. This same year Conway and Smith (8) reported on an extensive study of the application of NMR to the determination of oil in corn. They employed both means mentioned above for measuring the oil content and also made measurements on single kernels. For these latter measurements the standard 40-ml cell was replaced by a 2-ml cell equipped with a special holder for the kernel so that it could be held in the optimum position.

Within the last two years D. E. Alexander and co-workers (1,4) have reported on the application of NMR measurements on oats, corn and soybeans directed toward plant breeding and genetics of oil crops. The oil content of seeds can be measured without harm to the viability of the seed. This should be a great aid in selecting seed for experimental purposes and evaluating the results.

Measurement of Liquid and Solids

Liquid compounds containing hydrogen can be measured in the presence of solid materials. The wide-line NMR has been applied in the petroleum industry (9) to the control of oil-in-wax on a process control basis, and in the fat and oil industry to the determination of solids in fats, oils and shortenings (3,5,9,11,17) in connection with research problems. Those in the fat and oil industry usually think in terms of the solids present in a sample so that per cent liquid found is subtracted from 100 to obtain the solids content of a sample. The measurement of solids in fats and oil can be made over a wide range of temperatures from −15C to 80C if desired and solids content from 0% to 100% (3,12) can be determined, and compared to the usual dilatometric method, Solids Fat Index (SFI). The SFI is an index and not a true measure of solids and is limited to SFI values below 50 and measurements between 10C and 37.8C.

The application of NMR to fats, oils and shortening is more complex than moisture or oil content of a sample. When applied in this area information is usually desired on the solids content at selected temperatures. This involves obtaining equilibrium or close to equilibrium conditions between the liquid and solids at a given temperature in a reasonable time, an hour or less, and taking into account and correcting for the variation of the NMR measurement of the liquid portion with temperature.

Equilibrium of the liquid and solid in a fatty system can be attained more rapidly when approached from the solid side of equilibrium. This is accomplished by chilling the 5 g of liquid sample, in an acetone-carbon dioxide bath at −60C or lower for 15 min. Under these conditions all the glycerides solid at the testing temperature are in a solid state as well as most of the other glycerides. The sample is then placed in the bath maintained at the temperature at which the solids are to be measured. Equilibrium or close to equilibrium conditions are attained in 30 to 45 min and are usually within 1% to 2% of solids measured after 16 hr. For control purposes and most research applications measurements made within 30 to 45 min are usually adequate.

The NMR signal expressed in millivolts per gram of sample is proportional to the amount of liquid present. Thus NMR signal at a given temperature divided by the NMR signal for the liquid at that temperature times 100 will equal the per cent of liquid in a sample and this subtracted from 100 gives the per cent solids. The liquid glycerides absorb more energy as the temperature is lowered, so this must be taken into account when calculating the per cent solids. Most samples are liquid at 60C and the NMR signal strength for the liquid can be measured at this temperature or one at which the sample is liquid. The signal strength at a given temperature is inversely proportional to the absolute temperature as expressed in the following equation.

$$S = \text{constant} \times \frac{N \times H^2 \times \quad 3 \times I\,(I+1)}{T}$$

S = NMR signal strength in volts
N = Number of nuclei
H = Applied field strength
= Gyromatic ratio
I = Spin of isotope
T = Absolute temperature

The signal for the liquid portion can be corrected to the temperature of the sample and the signal for the sample divided by the corrected liquid value. The following equation includes the correction.

$$\text{Per cent solids TC} = 100 - \frac{ST \times (273.16 + T)}{ST_1 \times (273.16 + T_1)} \times 100$$

ST = S the NMR signal for the sample at temperature T in C.
ST_1 = S the NMR signal for the sample in the liquid state at T_1 in C.

This assumes that the glycerides, liquid at the testing temperature are the same as those in the liquid state at the higher temperature where the sample is liquid. They are not exactly the same and will differ slightly in hydrogen content and in a similar manner for most samples so further correction is not attempted or considered practical at this time.

In place of the equation a graph may be used from which the per cent solids may be read directly without a liquid measurement at 60C or in the liquid state. If the products being measured have similar liquid properties in the liquid state, NMR measurements can be made for example at 60, 70 and 80C and an average value can be used for extrapolation or calculation of the NMR signal for the liquid at lower temperatures. These values may then be plotted on a graph at 0% solids and a straight line drawn to zero signal at 100% solids (12). Then the per cent solids corresponding to a given NMR measurement can be read directly from the graph based upon the temperature at which the measurement was made.

Nuclear magnetic resonance measurements have been made on salad oil type products over the range of −15 to 0C where most of the samples were completely liquid (18). By this means it was possible to study the variations in solids content of the respective samples which appear similar at 0C or higher. The solids content of a variety of shortenings and some partially hydrogenated and completely hydrogenated vegetable oils have been measured over the temperature range of 10 to 40C. Products tested have ranged in solids content from 6% to 100% solids at 10C and 100% to 0% solids at 40C. As the temperature increases the per cent solids usually decreases but composition can be prepared where there is only a slight drop between 10 and 40C (11,18). At this point the question is usually raised as to what is the relationship between per cent solids by NMR and SFI values. While there is a general relationship between per cent solids and SFI values the variation is so great for different formulations that one cannot estimate one value from the other with any satisfactory degree of accuracy (11). This is not surprising when one considers the basis and conditions for determining the SFI values (11).

In addition to measuring the solids content of shortening samples or formulations over a wide range of temperatures, NMR measurements can also be applied to a finished product as it is produced or at any time after production. This is not possible by any other means so far as we know.

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