On-Stream NMR Measurements and Control[1]

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ABSTRACT

Four examples are described in which nuclear magnetic resonance (NMR) measurements provided quantitative analyses with an accuracy of 1% of the amount measured. In the first instance, the amplitude of the NMR absorption of hydrogen was combined with the weight and volume of the sample to give a moisture determination in starch. The second NMR instrument used no sample weight and the amount of moisture in a flowing stream of Milo maize was measured by means of only the amplitude of the NMR absorption of hydrogen. The third instrument used the second harmonic of the NMR absorption from hydrogen to measure the amount of moisture in a flowing process stream of starch or other hygroscopic material without weighing. The last example described how the amplitude and area of the aluminum and hydrogen NMR absorptions, respectively, can be combined to measure the per cent aluminum and per cent hydrogen in a flowing process stream, again without weighing.

INTRODUCTION

Nuclear magnetic resonance (NMR) measurements can be used to perform qualitative, quantitative and relaxation analyses. The qualitative analyses can be performed by the selection, for the nucleus being measured, of the proper ratio of the frequency and the magnetic field used to obtain the resonance absorption. That is, the Larmor equation

$$\frac{\text{Larmor frequency}}{\text{magnetic field}} = \frac{\text{nuclear constant}}{2\pi} = \frac{\gamma}{2\pi}\ \frac{\text{Hertz}}{\text{Gauss}} \qquad [1]$$

must be an equality for the nuclear constant (γ, the gyromagnetic ratio) chosen. For a magnetic field of 10,000 gauss, the resonant frequencies of most of the nuclei are in the range of 0.3 to 46 MHz or in the medium or high frequency part of the spectrum (1). By sweeping the frequency from 0.3 to 46 MHz and noting the spectrum or the frequencies at which resonant absorptions are found, a qualitative analysis can be made.

A quantitative analysis can be obtained since the magnetic susceptibility (1) of the nuclei being measured, χ_o, is proportional to the volume concentration of those nuclei, according to the relation:

$$\chi_o = Nm^2(I + 1)/3kTI \qquad [2]$$

where N is the number of nuclei per volume, m is the value of the magnetic moment of the nuclei, k is Boltzmann's constant, T is the absolute temperature and I is the quantum number for the spin of the nucleus which can have values of 1/2, 1, 3/2, etc. The susceptibility of the nuclear magnetic resonance absorption is given by the relationship (1),

$$\chi'' = \frac{\chi_o}{2}\left[\frac{1}{1 + (\omega - \omega_o)^2T_2^2 + \gamma^2H_1^2T_1T_2}\right] \qquad [3]$$

where ω is the Larmor frequency in radians per second, H_1 is the strength of the field from which the nuclei are absorbing energy and T_1 and T_2 are the relaxation time values. The power absorbed by the nuclei, P, is

$$P = 2\omega H_1^2\chi'' \qquad [4]$$

n'' is proportional to χ_o, and since χ_o is proportional to the number of nuclei per unit volume, a measure of the power absorbed by the nuclei can be used to determine the volume concentration of the nuclei being measured or give a quantitative analysis.

The relaxation analysis is obtained through the determination of the values of T_1 and T_2. An inspection of Equation 3 will indicate how the values T_1 and T_2 can be determined. If the value of H_1 is reduced to a level such that $\gamma^2H_1^2T_1T_2$ is much less than a unity, then the susceptibility χ''_{low} is

$$\chi''_{low} = [\chi_o/2]\ [\omega_oT_2]\ [1/1 + (\omega - \omega_o)^2T_2^2] \qquad [5]$$

where the subscript low is used to denote the condition for a low value of H_1. If the variable $(\omega - \omega_o)T_2$ is then allowed to take on values above and below zero, the absorption curve with a Lorentz shape is obtained (1). When the variable $(\omega - \omega_o)T_2$ is at a value equal to a unity, the amplitude of the susceptibility is 1/2 of the peak value. Thus, from the value of the width of the absorption line when H_1 is very small, the value of T_2 can be calculated from the equation

$$\text{Linewidth} = 2/T_2 \qquad [6]$$

To determine the value of T_1, the term $(\omega - \omega_o)T_2$ in Equation 3 is set to zero which makes the susceptibility χ''_{high} equal to

$$\chi''_{high} = [\chi_o/2]\ [\omega_oT_2]\ [1/1 + \gamma^2H_1^2T_1T_2] \qquad [7]$$

When H_1 is increased until $\gamma^2H^2T_1T_2$ is a unity, the NMR signal is half of its maximum value. The value of T_1 can be calculated from the equation

$$\gamma^2H_1^2T_1T_2 = 1 \qquad [8]$$

These relaxation times, T_1 and T_2, are the time constants for the rate at which the energy is gained or lost by the nuclei. Energy is coupled between nuclei of the species being measured at an exponential rate whose time constant is T_2. Energy is coupled to the remainder of the surroundings for the nuclei being measured by an exponential whose time constant is T_1. From these values of T_1 and T_2 much can be determined about interatomic distances, relative motions and binding energies, etc.

In many processes, it is desired to measure the quantities of particular constituents. NMR can be used to determine the quantities of different constituents containing different nuclei by using appropriate frequency-magnetic field ratios for each nucleus, and measuring the power absorbed by each nuclear species. Using Equation 5, the value of N for each species can be determined. If T_1 and T_2 remain constant at different values of N, a straight line of amplitude vs. per cent is obtained. Very often, however, the values of T_1 and T_2 change without a change in N. Unless new values of T_1 and T_2 are determined for each new measurement, errors can occur. These errors, caused by the

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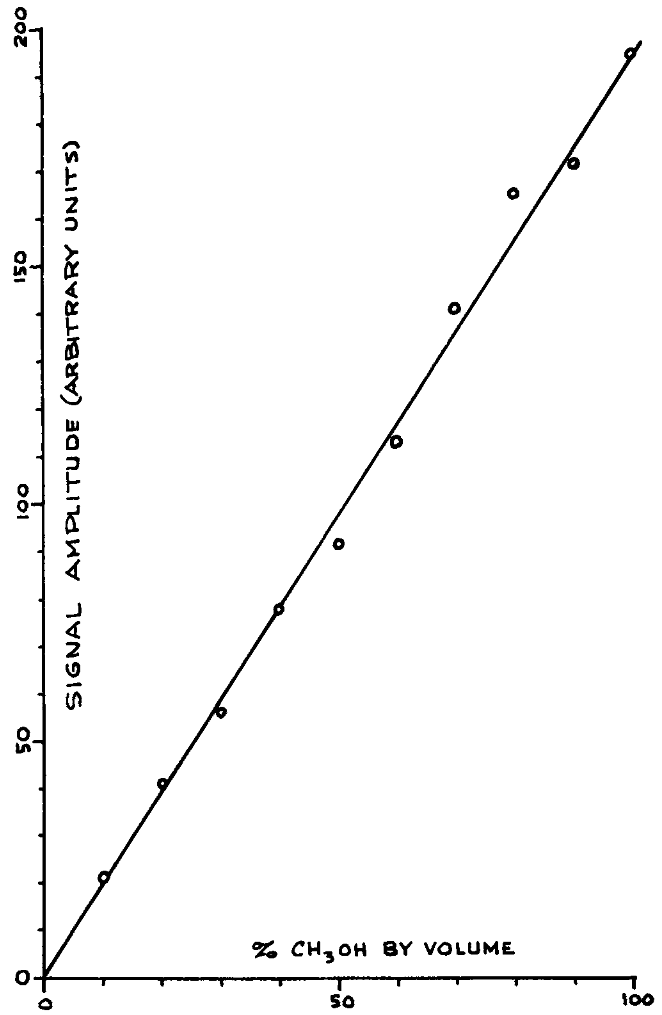


FIG. 1. Graph of NMR peak signal amplitude as a function of per cent alcohol in carbon tetrachloride.

variations in the relaxation times, can be reduced if the area under the absorption curve in Equation 5 is used rather than the amplitude at resonance or $(\omega - \omega_0)T_2 = 0$. The area contains the effect of all the nuclei rather than only those at the peak value and it is obtained by integrating Equation 5,

$$\text{Area} = [\chi_0]\ [\omega_0/2]\ [1/(1 + \gamma^2 H_1^2 T_1 T_2)^{1/2}] \qquad [9]$$

In Equation 9 the direct dependence upon T_2 has been eliminated. The remaining inverse dependence upon T_1 and T_2 can be reduced to the value desired by reducing the magnitude of $\gamma^2 H_2 T_1 T_2$ to be much much less than a unity.

The following paragraphs will show four instances in which NMR measurements were used to determine the quantity of one or more constituents in process streams and the different methods that were used. The first is the moisture measurement in starch. The second is the measurement of the moisture in a flowing stream of grain. The third is a moisture measurement on flowing hygroscopic materials without weighing. The fourth is the measurement of the amount of hydrogen and aluminum in a flowing process stream.

NMR DETERMINATION OF MOISTURE IN STARCH

Equation 5 shows that the peak value of the absorption curve, when $\omega - \omega_0 = 0$, could be used to measure the number of the nuclei if the density and the value of T_2 are constant or known values. If a standard volume is used, density can be controlled by weighing. If T_2 is constant over the range of the variation experienced, the graph of the peak of the absorption as a function of per cent of the variable is a straight line. To test this we made a mixture of methanol in carbon tetrachloride which should have a constant value of T_2 for all values. The graph of the peak amplitude of the NMR absorption as a function of per cent methanol is shown in Figure 1. The best fit for the data is the straight line shown.

If T_2 is not constant, the straight line dependence between the peak amplitude and the per cent concentration will not be obtained. However, if the variation with T_2 follows a specific curve, the curve can be used to calibrate the measurement of the constituent desired.

A valid question is, why not measure the value of T_1 and T_2 and correct the peak reading according to Equation 5? This is a good question and it would be a good thing to do. However, the measurements of T_1 and T_2 require procedures which are time consuming and not easily or inexpensively automated for adaptation to on-stream measurements. Then, why not integrate the area under the absorption curve? Here again, the integration requires time and added expense. Thus, the most rapid and continuous measurement that can be made on a sample by NMR is the peak amplitude of the absorption curve. In the next paragraphs it will be shown how this measurement was used, with a calibration curve, to determine the moisture in starch in which the value of T_2 varied predictably with the amount of moisture.

The NMR signal from all of the hydrogen in starch (2) with 0.5% moisture consists of two parts: a broad signal (9 gauss wide) from the hydrogen in the starch molecules, and a narrow signal (0.8 gauss wide) from the hydrogen in the 0.5% water. To measure only the hydrogen from the moisture, it is necessary to restrict the variable $(\omega - \omega_0)$ in Equation 5 to a value less than the broad signal centered on the narrower hydrogen signal. When this is accomplished, only the narrow absorption curve is measured and the NMR signal from the hydrogen in water is separated from the signal from the hydrogen in the starch.

The reason that there are two distinct hydrogen NMR signals from water and starch is that the values of T_2 are different for the hydrogen in each of the molecules. The T_2 values are dissimilar because the restrictions to the motion of the hydrogen are not the same. The values of T_2 vary with the amount of moisture because the restrictions to the motion of the hydrogen in the water in starch also change. Usually the area of the NMR absorption curve would be used to obtain a linear curve, but this would add cost and would increase measuring time. It was found that, although the amplitude of the moisture signal did not have a linear variation with per cent moisture, it did have a curve which was repeatable if the amplitude of the NMR signal was normalized by sample weight. The graph of the NMR amplitude (D_{max}) divided by the weight as a function of per cent moisture is shown in Figure 2 for a sample of starch. The graph is not a straight line because the value of T_2 decreases with decreasing moisture. The graph of signal area as a function of moisture should be a straight line.

Since the value of T_2 decreases with decreasing moisture, or the value of the linewidth increases according to Equation 6, it was also found that a repeatable curve could be obtained of the linewidth as a function of moisture, and that the linewidth doubled as the moisture varied from 6% to 16% (Fig. 2). It was found that both the amplitude vs. moisture and the linewidth vs. moisture curves were so constant for each type of starch that either the amplitude or the linewidth could be used to measure the moisture percentage. Two instruments were developed for the Corn Industries Research Foundation: the first was used to

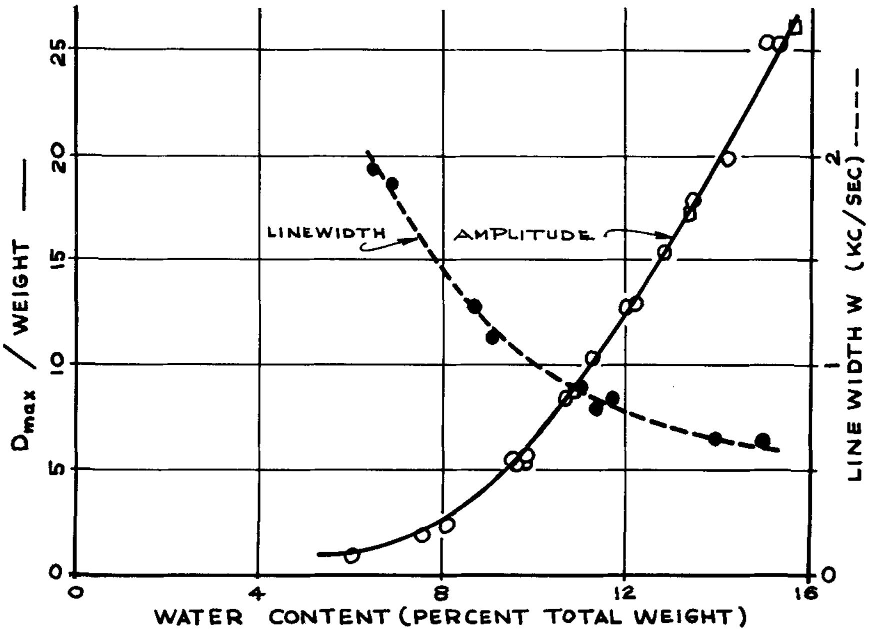


FIG. 2. The NMR amplitude and linewidth for the hydrogen in starch graphed as a function of the water content.

measure the moisture in starch by means of the amplitude of the NMR signal, and the second was used to measure the moisture in starch by means of the linewidth of the NMR signal.

NMR Amplitude Measurement of Moisture in Starch Samples

It was decided to provide an instrument which was specifically tailored for the measurement of moisture in starch over the range of 2% to 100%. Because the research work had been accomplished over a range of magnetic fields of 235 to 10,000 gauss, the sample size and field strength could be chosen to give the least cost of the magnet with a useful signal-noise ratio. If signal integration were used, the size and cost of the magnet could be reduced even further. In this manner, a magnetic field was chosen to give operation at 5 MHz with a sample size which could vary from 1/2 to 1 1/4 in.O.D. These characteristics were constructed into the developmental laboratory model (3). With this equipment a signal-noise ratio of 3:1 could be obtained without integration from the hydrogen in 11.95% moisture in starch. The signal-noise improvement of 100 by integration was such that measurements accurate to 1% of the reading could be made for moisture values from 2% to 100%.

With this instrument (3) the curves of Figure 3 were obtained for 12 types of starch, modified and unmodified. Each material has its own calibration curve and none are exactly the same. While measurements can be made within 1% of the value (for example 10 ± 0.1) on each calibration curve, one calibration curve for a limited range for all starch could be drawn which would enable a measurement of 10 ± 0.2 to be made. Two units were made for the Corn Industries Research Foundation for testing in 1954. These units were exact copies of the laboratory unit described (3). These units were tested for a year in different plants. The unit tested at Corn Products Refining Co. gave a 3 sigma error of less than 0.1% for the measurements made over the complete year at average moisture levels of 10%. Thus, the error was within the design limit of 1% of the amount measured. The results from the other test unit are not available for comparison. After this successful test, the plans for the unit were turned over to the Schlumberger Company for manufacturing.

From the results of the NMR measurements on starch it has been concluded that: (a) The NMR signal from the hydrogen in water can be separated from that from the hydrogen in the starch. (b) The amount of moisture in starch can be determined from a measure of the peak amplitude of the signal from the hydrogen in water if a calibration curve is used and the data are normalized by

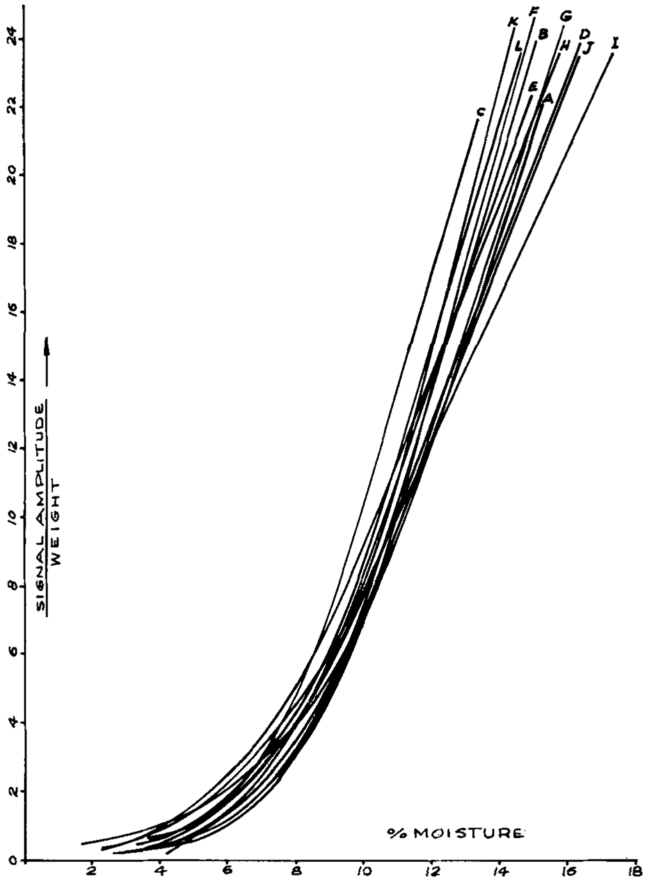


FIG. 3. Peak-to-peak amplitude of the NMR recording as a function of moisture for 12 types of starch, unmodified and modified. A, pregelatinized starch; B, starch ester; C, starch ester; D, oxidized starch; E, starch ester; F, oxidized starch; G, corn starch; H, corn starch; I, oxidized starch; J, corn starch; K, Buell Pearl starch; L, powdered starch.

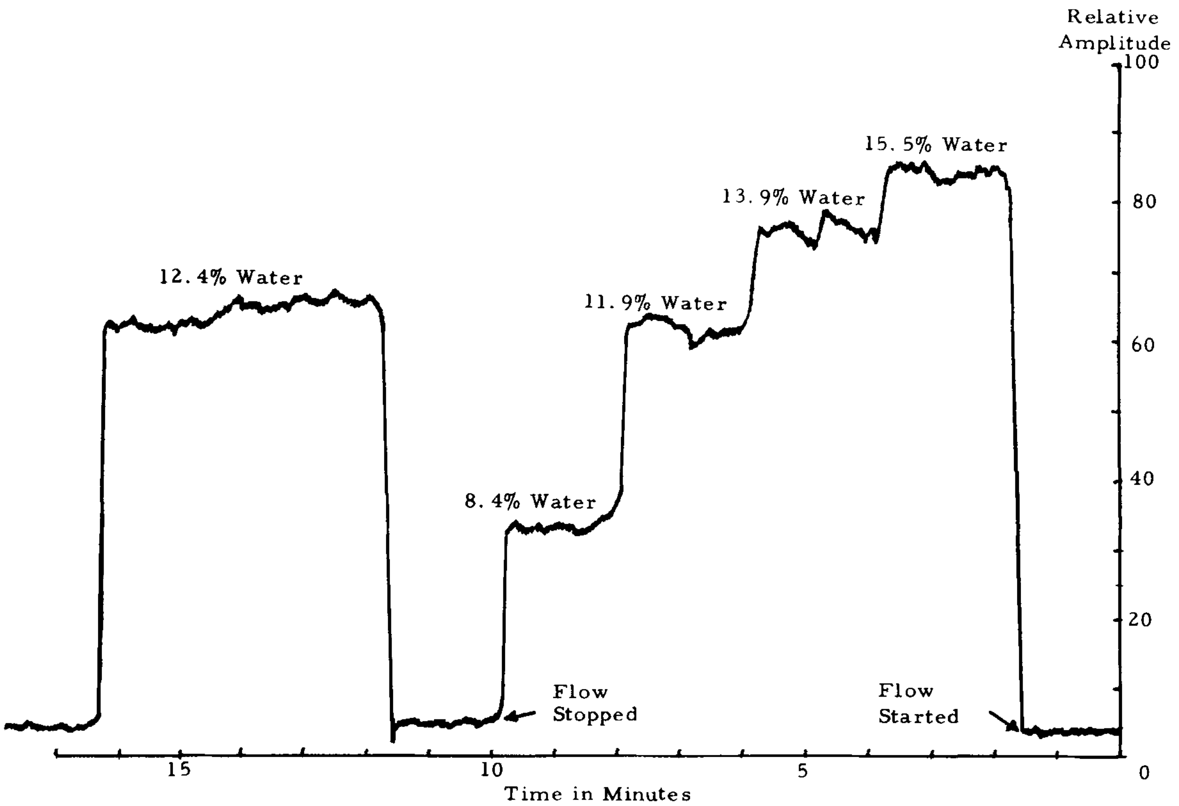


FIG. 4. Recording of the peak value of the NMR signal from the hydrogen in the moisture in flowing milo maize. Flow rate is 100 cc/min.

means of the weight of the sample. (c) The amount of moisture in starch can be measured from the area under the absorption curve from the hydrogen in water with only a calibration constant and a weight normalization. (d) The amount of moisture in starch can be determined from a measure of the linewidth of the signal from the hydrogen in water with a calibration curve.

To perform the second measurement, the weight of the sample shown by the detection coil had to be known. This requirement could be met if all of the sample were within the volume of the coil. The usual result was a loss in signal because the coil volume would not be completely filled, and such a decrease in signal-noise ratio would cause a reduction in measurement accuracy. Therefore, keeping the sample totally within and less than the coil volume was not recommended.

The recommended solution was to use a sample tube on which a constant volume was marked. A standard weight of starch was placed into the tube which was then vibrated until the starch level filled the volume mark. This gave a constant density for all samples which had an accuracy sufficient to make moisture measurements within ± 0.1%. This technique was introduced and perfected by Tom Conway of Corn Products Co. To determine the per cent moisture with this constant density technique, the calibration curve has to be applied only to the peak amplitude of the NMR signal from the hydrogen in water, not to the value normalized by the weight. This procedure greatly simplified the calculation of moisture from the NMR data because a division by weight was not needed and it increased the signal-noise ratio.

NMR MOISTURE MEASUREMENT ON FLOWING MAIZE

As a second part of the program for the Corn Industries Research Foundation, moisture measurements in milo maize were made with the NMR instrument used for starch, so that the measurement could be made on a flowing stream rather than on discrete samples and the density would be fairly constant.

The remaining problem was the interference of the hydrogen signal from the oil in the germ. If the widths of the NMR signals from two different hydrogen-containing materials differ by a factor greater than 10, the effect of the hydrogen giving the broadest signal can be eliminated from the measurement of the narrow signal by restricting the scan of the magnetic field over only the narrow signal. Thus, the narrow signal can be selected from the broad signal as in the case of moisture in starch.

The case of oil and moisture in the grain presents a different problem. The narrowest signal in grain comes from the hydrogen in oil, the broadest signal comes from the hydrogen in starch and protein, while the desired signal from the moisture has a width between the other two. Therefore, limiting the width of the scan will not separate the water signal from the oil signal because the water line is wider.

Another possibility exists for the separation of these two signals. The signal from oil and water will consist of the sum of two absorption curves so that the peak value will be, from Equation 5,

$$\text{Peak} = K_1N_1 \left(\frac{T_{21}}{1 + S^2T_{11}T_{21}}\right) + K_2N_2 \left(\frac{T_{22}}{1 + S^2T_{12}T_{22}}\right) \quad [10]$$

where $S = \gamma H_1$ is the value of the saturation constant, K_1 and K_2 are constants of the water and oil detection, T_{21} is the value of T_2 for water, T_{11} is the value of T_1 for water, T_{22} is the value of T_2 for oil, T_{12} is the value of T_1 for oil, and N_1 and N_2 are the amounts of oil and water. It should also be understood that the T_1 values are nearly equal but that T_{21} (water) is much shorter than T_{22} (oil). The effect of the oil on the peak signal can be reduced by changing the value of S by controlling H_1. Since the values of T_2 are different, the peak signal can be made mostly from the moisture signal, by controlling H_1. That is, the oil signal will be saturated (made small) while the water signal will be

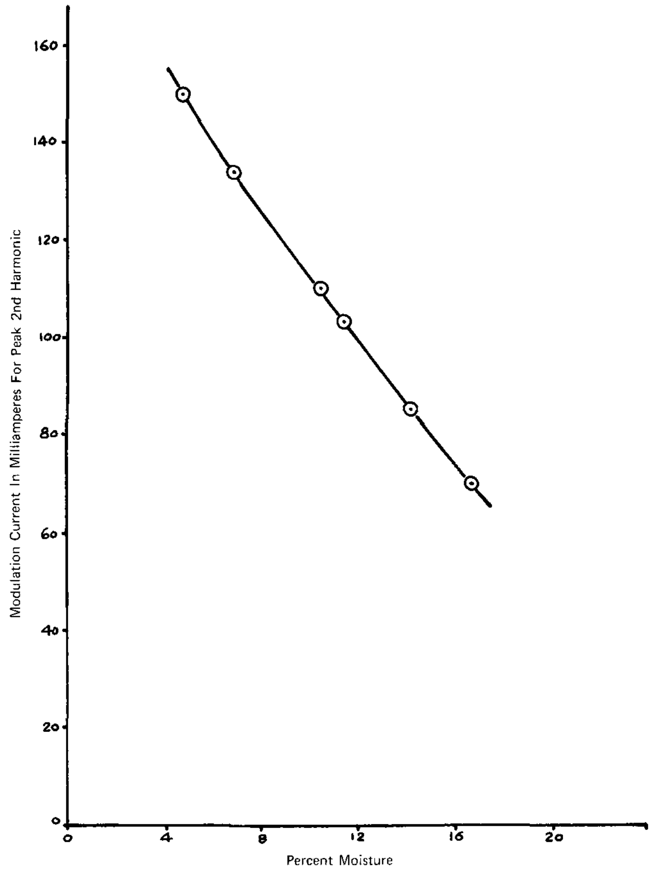


FIG. 5. Modulation amplitude, H_m, for the maximum of the peak second harmonic versus moisture content for starch.

relatively unchanged. This saturation method of measuring the moisture signal separate from the oil signal was used in the equipment and experiment to be described for flowing milo maize.

The Southwest Research Institute Laboratory NMR Moisture Measuring equipment (3) was modified to accept a plastic pipe through the detection coil. The top of the pipe was connected to a funnel-shaped hopper into which the maize was stored. Another container was placed below the pipe to catch the grain as it flowed through the pipe from the hopper. A valve at the bottom of the pipe was used to regulate the flow of maize to 100 cc/min.

The NMR equipment was adjusted so that the peak value of the hydrogen NMR signal could be measured. The equipment stability was such that this measurement could be obtained without readjustment for 10 to 20 min. The value of H_1 was increased until the oil component in the NMR signal was saturated. After stability was reached, the maize would be allowed to flow through the pipe. The recording of the peak level shown in Figure 4 was obtained for one run. Grains with moisture values of 8.4%, 11.9%, 13.9% and 15.5% were available. These samples were passed sequentially through the flow tube to give the recording shown in Figure 4. Then all of the samples were mixed together to obtain the results shown in the last part of the recording in Figure 4. Also shown in the signal level obtained from the empty detection coil.

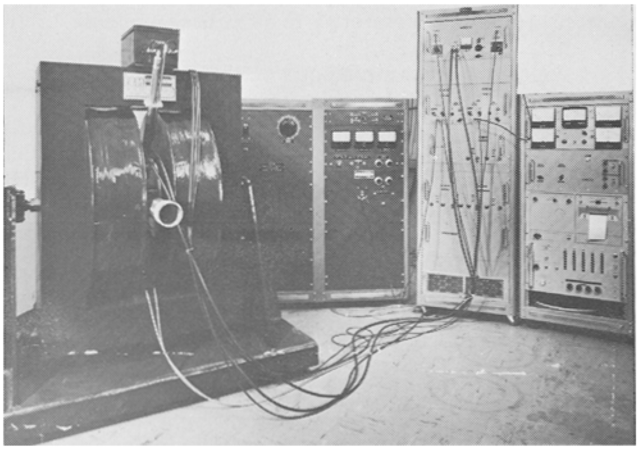
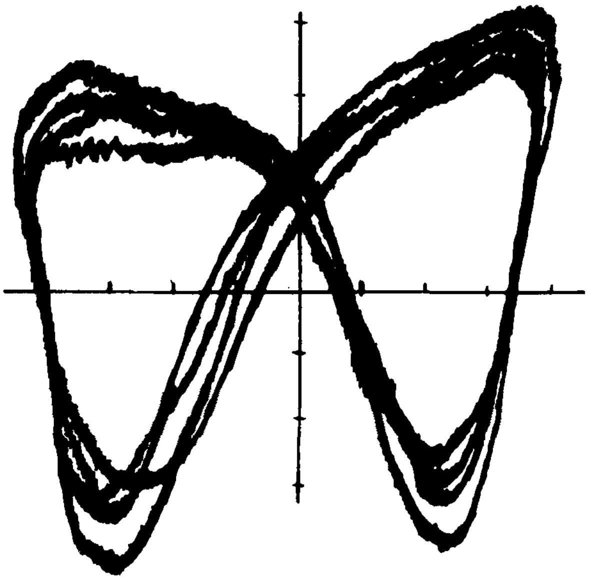
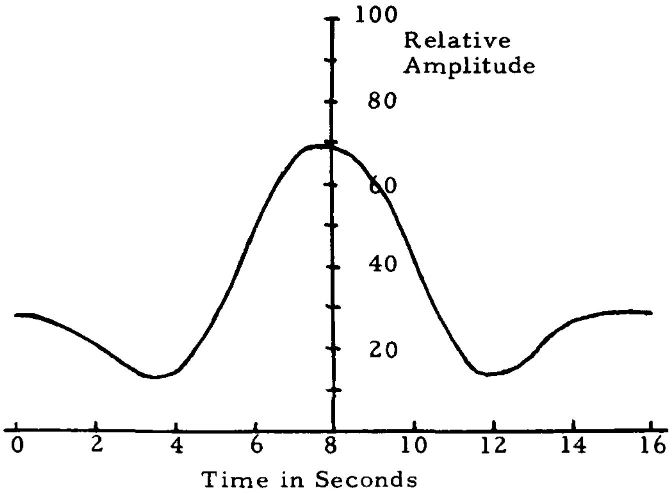


FIG. 6. NMR equipment developed at Southwest Research Institute to measure the aluminum in a 3 in. diameter flowing process stream.



a. Aluminum Absorption Signal



b. Graph of Second Harmonic of Aluminum Absorption Signal

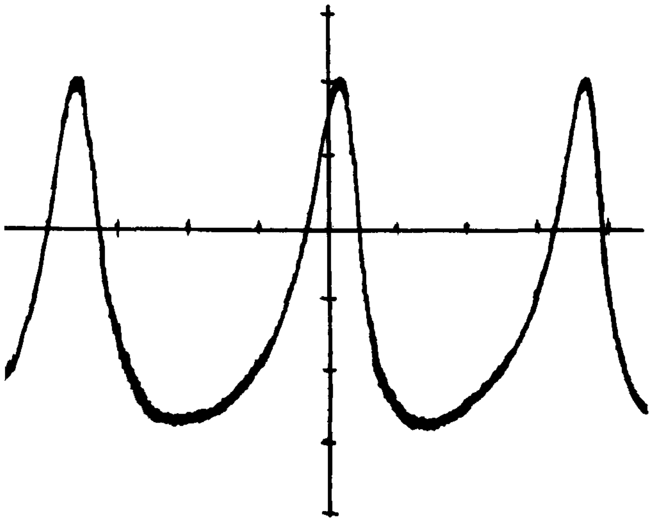
FIG. 7. Aluminum signals from the equipment in Figure 6.

These results demonstrate that NMR peak amplitude measurements of moisture can be made on flowing process streams, that saturation level settings can separate the NMR hydrogen signals from oil and water, and that a restriction of the scan (variation of the amount of signal scanned) can be used to separate the oil plus water hydrogen signal from the hydrogen signal from the starch and protein.

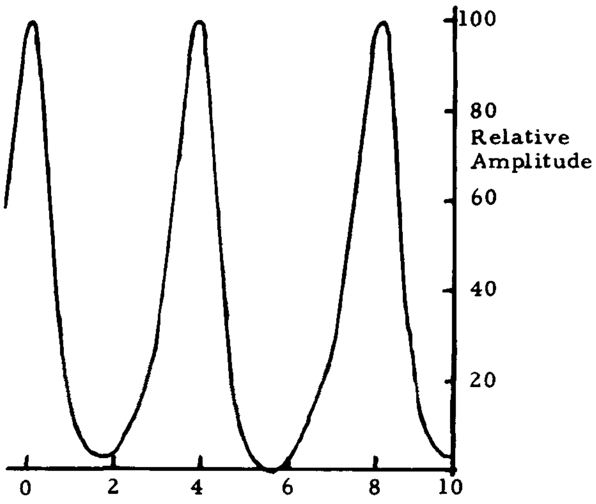
NMR MOISTURE MEASUREMENT IN FLOWING HYGROSCOPIC MATERIALS WITHOUT WEIGHING

It was shown in Figure 2 that not only the amplitude of the NMR signal from the hydrogen in the moisture in starch

FIG. 8. NMR equipment developed at Southwest Research Institute to measure the amount of hydrogen in a 3 in. flowing process stream.



a. Hydrogen Absorption Signal Without Signal/Noise Improvement



b. Graph of Hydrogen Absorption Signal With Signal/Noise Improvement

FIG. 9. NMR hydrogen signals from the equipment in Figure 8.

varied nonlinearly with per cent moisture, but also that the width of the NMR absorption signal varied nonlinearly. Therefore, as stated previously, the measurement of the linewidth could also be used for determining the amount of moisture in starch. Research work showed that a calibration curve could be obtained for each type of starch, and that the calibration curves for many types were identical.

A moisture meter (4) using the measurement of the width of the NMR absorption curve at half amplitude was constructed and tested as a part of work supported by the Corn Industries Research Foundation. It was found that the linewidth varied not only with the amount of moisture but also with the value of the radio-frequency field, H_1, and the rate of the variation through the signal. The value of H_1 and the rate were held constant. As has been described (1), to improve the signal-noise ratio a lock-in detector should be used. The resulting signal output from this system is shaped like the first derivative of the NMR absorption curve. It is difficult to hold the magnetic field at the value required to give the peak of the derivative curve proportional to the peak of the absorption curve. Therefore, it was decided that the first derivative signal would be used as an error voltage to hold the magnetic field at the resonance value by means of a feedback (4). To obtain a measurement, the second derivative of the absorption curve was used (4); however, it was not necessary to make the derivative since the amplitude of the first harmonic of the modulation, when selected by a phase-sensitive or lock-in detector, provides the first derivative curve. Similarly, the second derivative curve is obtained from the amplitude of the second harmonic of the modulation. The magnet is locked to the resonance value by using the amplitude of the first harmonic as an error curve, and the feedback causes the zero position of the first harmonic to be held within the limits of the feedback gain. When the first harmonic is at its null value, the second harmonic is at its maximum value for measurement.

When the lock-in system was used and the amplitude of the second harmonic was graphed as a function of modulation amplitude, a series of curves were obtained. It was found that the second harmonic amplitude would reach a peak value of 35% of the absorption amplitude when the peak amplitude of the modulation reached a value of 2.2 times the linewidth, W. When the values of the modulation amplitude required to produce the peak values were graphed as a function of the per cent moisture, the curve of Figure 5 was obtained. Thus, the value of the modulation current could be monitored to provide a measure of the percentage moisture.

A continuous measurement would be obtained by a zero point from a second derivative for a servo mechanism. That is, if the modulation amplitude were, in turn, modulated at a lower frequency, and the first harmonic of this modulation-of-the-modulation were measured by a phase sensitive detector, another curve with a zero crossing would be obtained. The zero-crossing at $H_m/W = 2.2$ could then be used as an error curve for the desired servo-control.

The NMR instrumentation to measure a quantity directly proportional to the width of the NMR signal can be used to measure the amount of moisture without a weight determination. This is because the width is measured regardless of the magnitude of the NMR signal as long as sufficient material is in the coil to give a signal-noise ratio sufficient for the accuracy desired. Moisture measurements with the equipment described can be used on many hygroscopic materials, i.e., without weighing, in discrete samples, in flowing process streams, within 1% of the value measured, (10 ± 0.1%), with either a calibration curve or a calibration constant.

HYDROGEN AND ALUMINUM NMR MEASUREMENTS ON A FLOWING PROCESS STREAM

NMR moisture measurements have been made in starch with a weight measurement and a calibration curve, in flowing grain without a weight measurement; and in starch without a weight measurement. Additional information involves the design, development and test of the amount of hydrogen and aluminum. These measurements were made on a flowing process stream 3 in. in diameter in which the material flowed at a rate of 100 lb/min. The material was a thick, viscous mixture which required 250 psi to pump.

Experiments showed that the linewidth of the aluminum signal was 16 gauss and did not change with the amount of aluminum. On the other hand, the linewidth of the hydrogen signal varied with concentration and other factors. The amplitude of the second harmonic of the NMR absorption should be measured to determine the amount of aluminum without weighing, and the area under the hydrogen NMR absorption curve should be measured to find the amount of hydrogen without weighing. With such measurements voltage readings proportional to the aluminum NMR signal amplitude and to the hydrogen NMR signal area could be directly calibrated in terms of aluminum and hydrogen per cent, respectively.

Measurement of Aluminum

The aluminum NMR system is shown in Figure 6. A magnetic field of 10,000 gauss placed the aluminum resonance frequency at 11.094 MHz. The first harmonic signal from the aluminum was used as an error signal to keep the intensity of the magnetic field and the frequency of the transmitter at the resonance value for aluminum of 1,109.4 Hertz per gauss. The modulation at 18 Hz had an amplitude of 2.2 times the linewidth of the aluminum NMR signal or 35.2 gauss. Thus, when the second harmonic of the NMR signal from aluminum was measured it was at its peak value and could be used to determine the amplitude of the NMR absorption signal from aluminum.

The equipment constructed to measure the magnitude of the second harmonic of the NMR signal from the aluminum in the 3 in. process is shown in Figure 6. The 3 in. diameter pipe for the process stream through the magnet is clearly visible. The shorter rack of equipment on the right side of the Figure records the data. The voltage proportional to the percentage of aluminum is given on the top meter on the left side of that rack. The variation in per cent of any preset value is shown on the bottom meter on the left side of the rack with full-scale readings selected at values of either 1% or 5%. The digital recorder sequentially records the percentage of aluminum and the percentage of hydrogen at a rate of one record every second.

The aluminum NMR absorption signal obtained is shown in Figure 7a. Two signals are actually presented with the sinusoidal modulation voltage applied to the horizontal axis. The Lissajous figure shows that a signal is obtained during both the positive and negative slopes of the modulation giving two absorption signals for each modulation cycle. When the absorption signals shown in Figure 7a are fed into a phase detector with a reference signal at 36 Hz (twice the modulation frequency), the second harmonic signal shown in Figure 7b is obtained as the magnetic field is varied through the signal. The shape of this aluminum second harmonic signal has been described (4). When the magnetic field is locked to the aluminum frequency, the output of the aluminum system is a voltage proportional to the peak amplitude of the second harmonic of the aluminum NMR signal. This second harmonic amplitude is directly proportional to the magnitude of the peak of the aluminum NMR absorption curve which, in turn, because T_1 and T_2 are constant, is proportional to the number of aluminum nuclei in the sampled volume. Since the density was measured by another means already used on the process stream, the second harmonic amplitude could be calibrated directly in aluminum per cent with a correction factor from the density measurement; a weight determination was not needed.

With this calibration, and with a constant density, it was calculated that the accuracy of the NMR measurement of aluminum should be 1% of the amount of aluminum. That is, at 10% aluminum the measurement should be made as 10 ± 0.01%. The actual accuracy, measured as the 3-sigma values from a graph made from an 80 hr run, was ± 0.7% the amount of aluminum, or 10 ± 0.07%.

Measurement of Hydrogen

The hydrogen measuring system used on the 3-in. process stream is shown in Figure 8. The system used is much the same as that used for the aluminum measurement shown in Figure 6. However, there are significant differences. First, the magnetic field is 1000 gauss which makes the hydrogen resonant frequency at 0.00000 MHz.

Secondly, since the linewidth of the hydrogen signal is of the order of 0.1 gauss, the inhomogeniety of the magnetic field should be less than 50 milligauss over the sample volume which is 3 in. in diameter and 6 in. long. This requirement could only be met by a pair of coils with the Helmholtz spacing, a buildup-width ratio of 1.0776, an inside diameter of 19 in. and an outside diameter of 36 in. When these magnet coils were constructed and tested, it was found that with a spacing slightly less than the Helmholtz value an inhomogeniety of 30 milligauss was obtained over the sample volume.

The third difference was that the signal from the sample to be measured, rather than a reference sample, could be used to lock the frequency and the magnetic field together at the hydrogen resonance value of 4.257.76 Hertz per gauss.

The last difference was that the area under the hydrogen NMR absorption signal must be used rather than the amplitude because the linewidth varies with not only the amount of hydrogen but also other conditions. Therefore, a curve of linewidth versus hydrogen could not be obtained.

The equipment constructed to perform the determination of the area under the hydrogen NMR absorption curve from the 3 in. flowing process stream is shown in Figure 8. The detection coils around the 3 in. pipe carrying the flowing stream are clearly visible inside of the Helmholtz coil magnet to the right of center of the photograph in Figure 8. The tall rack on the left is the signal processing equipment while the one in the center is the magnet power supply.

The hydrogen NMR signals obtained from the detector are shown in Figure 9a. The signal-noise ratio is about 40:1. To make a measurement with the accuracy required, this signal-noise ratio had to be improved. The NMR hydrogen signals after signal-noise improvement are shown in Figure 9b. When these signals are passed through an integrator, a direct current voltage proportional to the area under the hydrogen NMR absorption curve is obtained. This value, in turn, is proportional to the number of hydrogen nuclei in the sample. Multiplication by a constant will then give the value related to the per cent of hydrogen for a fixed density. Again, the density measurement can be used as a correction factor and the weight of the sample need not be measured.

When constant density was assumed, the accuracy calculated for the hydrogen measurement was 1% the amount of hydrogen or 10 ± 0.1%. The 3-sigma values for the 80 hr run previously mentioned was 0.2%, or 10 ± 0.2%. Thus, the equipment exceeded the target accuracy both for the hydrogen and for the aluminum measurement.

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