SYMPOSIUM: WIDE-LINE NUCLEAR MAGNETIC RESONANCE (NMR)

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The PAT-20, Varian's New NMR Process Analyzer[1]

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ABSTRACT

Varian's earlier process analyzer, the PA-7, is now being replaced by a new solid state instrument, the PAT-20, with improved reliability and performance and simplified operation. The instrument measures the NMR signal of the protons in the sample, integrating the narrow line to give a quick and accurate quantitative analysis of water or oil in a previously weighed sample. The result can be displayed on a recorder or on a digital readout. It can also be fed directly into a computer for on line process regulation. A short description of the construction of the instrument is given and the principles of operation are explained.

INTRODUCTION

A Nuclear Magnetic Resonance (NMR) Process Analyzer known as the PA-7 and originally designed by Schlumberger Well Surveying Corporation has been used for many years in process analysis and control and in plant breeding research. Many of the papers of this symposium describe analyses made with this instrument (1-6).

The NMR process analyzer uses the principles of NMR (7) to measure the number of protons in the liquid part of the sample. This number can easily be related to moisture or oil content or liquid-solid ratios using an appropriate standard sample. Moisture analysis has been made in cereals, sugar, cheese and other food products, paper, wood, textile fibers, tobacco, detergents, etc. Fat analysis has been made in cocoa and dry milk; oil analysis in geological samples and seeds. Liquid-solid ratio analysis has been made in margarine, shortening and other fats, waxes, slurries, pulp, etc. Time dependent change of a liquid into a solid, e.g., the hardening of an epoxy resin, can also be studied thanks to the rapidity of the measurement. The measurement is nondestructive, which is demonstrated by planting the seeds measured to have the highest oil content and obtaining a crop richer in oil (6).

During the many years since the PA-7 was designed, the technique for building NMR instruments has developed significantly. Taking advantage of all these improvements, a new process analyzer, the PAT-20, has been designed. This paper will describe the principles of operation and the construction of the new instrument.

Principles of Operation

The basic phenomenon of NMR has already been described (7). A block diagram of the PAT-20 spectrometer

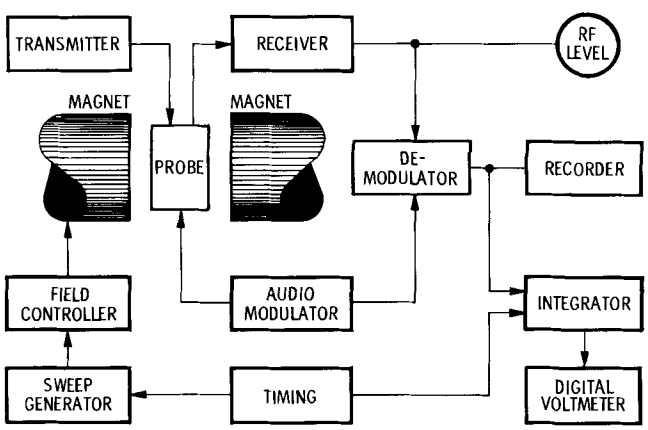

FIG. 1. Block diagram of the PAT-20.

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

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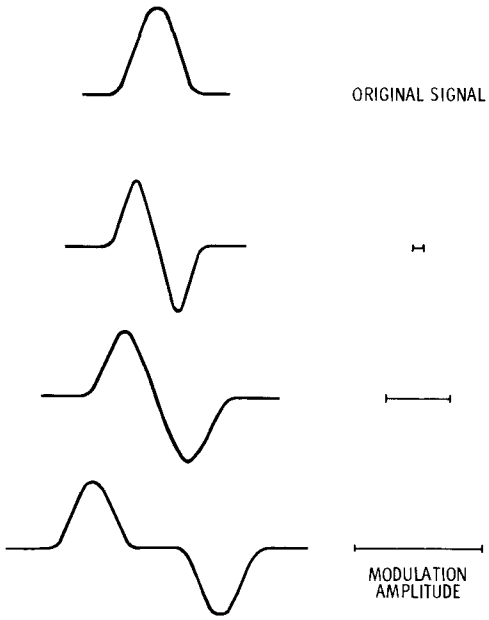

FIG. 2. Spectrometer signals.

with units needed to perform the NMR measurements is shown in Figure 1. The sample is inserted into the probe between the pole caps of the magnet. Radio frequency (r-f) energy is fed from the transmitter to a coil around the sample and the energy loss caused by resonating nuclei is detected and amplified by the receiver. Sensitivity is considerably enhanced by modulating the magnetic field with some extra coils in the probe and detecting signals containing only the modulation frequency in the demodulator. The resonance signal is integrated and the result is presented on the display of the digital voltmeter. The signal can also be traced on a recorder. A timing unit starts the integrator at the same time as it starts the sweep through the resonance. The current from the sweep generator goes to magnetic field sweep coils via the field controller which also keeps the field extremely stable by compensating for any environmental disturbances.

The shape of a resonance absorption signal is shown at the top of Figure 2. In many cases it would be too weak to detect directly. The signal-noise ratio is considerably improved by use of the described modulation technique. A small modulation amplitude gives a spectrum on the recorder like the second trace in Figure 2. This is approximately the derivative of the absorption line and ought to be integrated twice to give the area under the absorption line which is proportional to the number of resonant nuclei in the sample. Often, in wide line NMR one is interested in qualitative and not quantitative properties; then it is preferable to work in the derivative mode. In the process analyzer, where the quantitative result is important, one can preserve the absorption line shape by using overmodulation to obtain sidebands as shown in the bottom trace of Figure 2. These need only be integrated once (the second sideband signal is flipped over and added to the first) and thus integral accuracy is retained. Square wave modulation is used in the PAT-20 to avoid distortion of the sideband signals. The proper modulation amplitude should be larger than the total width of the narrow line to be measured, but not too much larger, since the larger it gets the more signal will start to be picked up from the broad line which comes from the solid portion of the sample.

Construction of the PAT-20

The process analyzer will be described from the user's point of view rather than from that of the engineer. It is housed in a single console with the magnet in a compartment at the right, below the writing desk, and the electronic circuitry contained in modular units at the top.

The magnetic field of 3500 gauss is obtained from a permanent magnet. By removing the small cover on the

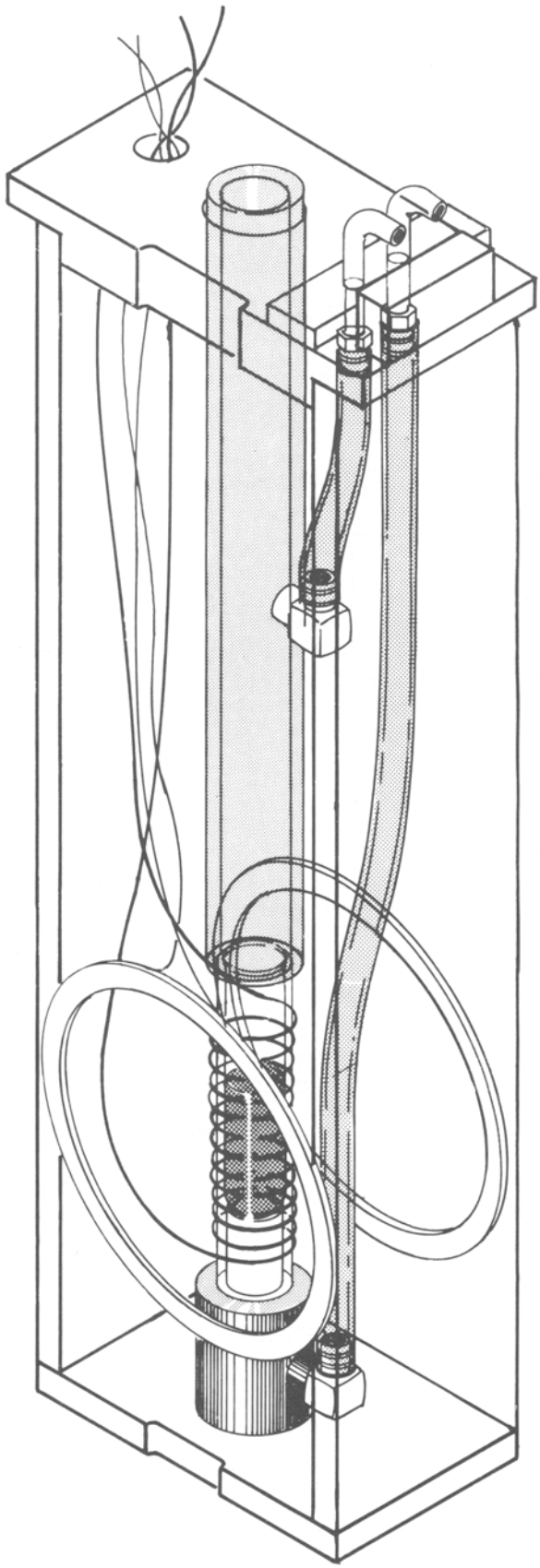

FIG. 3. The 2 ml probe.

desk, access is obtained to the magnet air gap for sample introduction. The design of the magnet is such that there is easy access to the air gap for installation of specialised probes if such are designed, e.g., for variable temperature control or on stream measurements.

The probe (the coil assembly) is shown in Figure 3. Two types are available, one for sample tubes of standard outer diameter 12 mm holding 2 ml samples and one for 32 mm sample tubes holding 30 ml samples. These sample volumes are well contained in the homogenous portion (darker area in Figure 3) of the r-f coil. Sample volumes smaller than the nominal value give accurate readings, but larger volumes cannot be accurately measured. A pair of larger coils in Figure 3 are used to obtain the field modulation. The sample is ejected from the magnet gap with the help of an air stream. Compressed air is introduced through the right tube at the top and pushes the sample up over the opening where the air leaves through the left tube. The sample tube rests on the air cushion and can easily be exchanged. When the next measurement starts the air is withdrawn and the sample drops into position in the r-f coil.

The electronics are built into modular units using current designs and are all solid state for extreme reliability. Should a malfunction occur the modular units are easily accessible for service and the faulty printed circuit card can be quickly replaced which minimizes downtime.

A unit to the right contains the r-f transmitter which oscillates at 15 MHz. The power to the r-f coil can be attenuated with the help of the switches in the row at the bottom in order to prevent saturation or to separate the oil signal from the water signal as described (7). The r-f receiver is located close to the probe but its gain is set by the knob and read on the meter on the transmitter unit. For some types of samples it may be necessary to retune the receiver by a knob in the sample introduction area.

The modulator and demodulator are housed in the large electronics controller unit. There are also the sweep generator, the integrator and the timing circuitry. The controls are used to set the proper modulation amplitude (including amplitudes for wide line studies of the solid signals), the sweep time (1 to 100 sec), the sweep width (also for solid signals), the noise filter time constant and the amplitude of the output signal. On the controller are also the start button and a switch for different modes of operation. In the lower part of the panel are seldom used adjustment controls for the resonance field and the zero of the integrator plus a switch to display certain voltages on the digital voltmeter.

The second unit from the left is the field controller. It compensates against any changes in the field caused by noise or transients in the electronic circuitry or by varying environmental temperature and assures a linear sweep of the magnetic field.

The unit to the left is the digital voltmeter. It displays the result (the integral) with three significant figures on digital readout tubes. When the result has to be compensated for the weight of the sample, the weight can be set to four figures and the digital voltmeter will display the compensated result. An optional device makes it possible to set a level under or over which the spectrometer gives a reject signal for the sample.

Connections are available at the side of the console for input and output of data and signals to make the process analyzer as versatile as possible. A strip chart or an X-Y recorder can be attached for recording spectra or an oscilloscope can be attached to monitor the signal. A printer can be connected to print out the results from the digital voltmeter. Sweeps and start signals can be fed to the spectrometer from a computer or other external device. All the voltages and signals are also fed to the pins of Burndy contacts which makes it easy to integrate the PAT-20 in a computerized system. Also, the air-controlled sample handling makes it easy to integrate the PAT-20 in an automated sample handling system.

Operation of the PAT-20

The operation of the process analyzer is very simple. Once the measurement parameters are set, insert the sample, dial in the weight if necessary, press the start button, note the integral value, remove the sample. The measurement parameters are set for every type of sample and should not be changed within a series of measurements. Only a few of them need to be changed when a different type of sample is to be measured, e.g., when changing from oil content to moisture content measurements. The parameters are r-f attenuation, modulation amplitude, sweep time, sweep range, time constant and signal amplitude. The last parameter should be changed so that large integral values are obtained in order to detect small relative changes in the results for different samples.

The results are calibrated with the help of a standard sample which preferably should be of the same type as those to be measured. The integral reading for the standard sample is compared with the known oil or water content of the sample, and the oil or water content in the unknown samples is found out by using the same ratio. To avoid this calculation the signal amplitude can be adjusted so that the integral for the standard sample becomes equal to the number describing the oil content in percentage or weight. Then all subsequent measurements will give a reading directly in percentage or weight. In some types of samples a strictly linear relationship between oil or water content and signal intensity does not exist and in these cases a calibration curve is needed.

For a large sample series it is convenient to use the process analyzer in the automatic mode. In this mode the sample is automatically ejected after the measurement and rests on the air cushion for a number of seconds. During this period the integral can be noted down and the sample changed. When the predetermined number of seconds have elapsed the sample automatically drops down into the probe and the next measurement is started.

ACKNOWLEDGMENTS

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