An On-Line NMR TechniqueWith a Programmable Processor*

K. Razazian
J. P. Bobis†
S. L. Dieckman
A. C. Raptis

Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

†Northern Illinois University
DeKalb, IL 60115

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K. Razazian, S.L. Dieckman, A.C. Raptis
Argonne National Laboratory Argonne, IL 60439
J P. Bobis Northern Illinois Univ. DeKalb, IL 60115
Tel: 708-252-7397 FAX: 708-252-3250

ABSTRACT

Nuclear magnetic resonance (NMR) spectroscopy is used to determine molecular content of materials, mainly in laboratory measurements. The reduced cost of fast computer processors, together with recent break throughs in digital signal processor technology, has facilitated the on-line use of NMR by allowing modifications of the available technology.

This paper discribes a system and an algorithm for improving the on-line operations. It is base on the time-domain NMR signal detected by the controller and some prior knowledge of chemical signal patterns. The desired signal can be separated from a composite signal by using an adaptive line enhancer (ALE) filter. This technique would be useful for upgrading process procedures in on-line manufacturing.

INTRODUCTION

NMR spectroscopy is the study of the magnetic properties of nuclei and the relationships of those properties to nuclear structure of matter. One of the most common methods to detect the NMR signal is by a pulsed NMR experiment. In this technique, the NMR signal can be observed by an additional oscillating magnetic field that is perpendicular to the external static field. When the frequency of the oscillating field is adjusted to match the spinning nuclei, torque on the precessing angular moment of magnitization vector causes the vertor angle to change with its static field. This transition, known as the NMR spectrum or relaxation time of nuclei, results in a net bsorption of energy by protons, which can be detected electrically. Data received by this time domain phenomenon can provide much information on the chemical properties and contents of materials. To implement the operation a portable NMR controller based on the TMS320C30 digital signal processor (DSP) chip has been developed. The controller transmits a RF signal to a sample in a large homogeneous magnetic field, and the resonance absorption of the radio frequency signal is detected in real time. Based on a some prior knowledge of the desired signal, an adaptive line enhancer filter is used to suppress the unwanted signals. The ALE filter is a special form of adaptive noise canceller designed to restrain the interference component of input while passing the desired signal. It consists of an interconneced delay element and adaptive filter. The adaptive filter output is subtracted from the input signal to produce the estimation error, which can then be used to update the tap weights of the filter. Output of the adaptive filter is used to display the existence of known chemicals and their concentrations.

Theory

The theory of NMR is complex and requires an extensive understanding of quantum mechanics. While the main focus of this paper is not to describe NMR theory, a modest explanation of the basic theory will be useful for understanding the hardware design.

Based on quantization theory, if nuclei are placed in an external magnetic field (B_0), they will eventually align with the direction of the field and exhibit a circular motion about the magnetic field (conventionally, the z axis). The frequency at which nuclei spin, called the Larmor frequency is directly proportional to the magnetic field

$$\omega=\gamma*B_0 \qquad (1)$$

where γ is the gyromagnetic ratio defined as the moment divided by the angular momentum[ex pulse Nmr]. For example, the Larmor frequency of a proton in a magnetic field of 1 Tesla is equal to 42.577 MHz.

Now consider applying an external magnetic field to a sample. Initially the nuclei are in state of randomness (Fig 1), but over a period of time the protons become partially oriented in the direction of the field and attain some degree of alignment M_z.(magnetization vector). This development is known as Longitudinal relaxation time and forms an exponential curve with a time constant T_1.

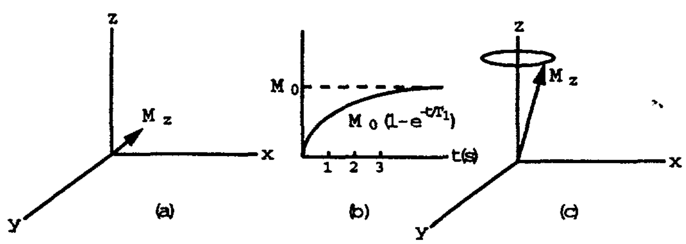

Fig..1. (a) Initially in random orientation (b) Time for proton to align with field B_0.(c) Vector representation of (b).

In a pulsed NMR experiment, an additional magnetic field B_1 is employed to a sample at its Larmor frequency causes the magnetization vector to rotate. For instance after a 90° pulse is applied (Fig. 2), the magnetization vector M_z lies along the x axis. After this transition, M_z begins to decay as the system comes back to equilibrium and to regrow along the z axis direction again. During this process, the magnetization will induce a decaying sinusoidal voltage (free induction decay, FID) at the rate of $\exp(-t/T_2)$ in a pickup coil in the x-y plane.

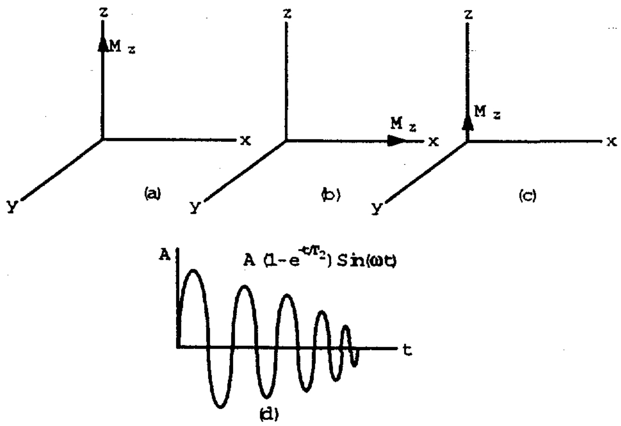

Fig. 2.(a) Sample in magnetic field (b) M_z after 90° pulse (c) M_z regrows along the z-axis (d) Free induction decay

The time constant T_2 (known as Transverse relaxation time) of the decaying sinusoidal signal or FID depends directly on the chemical contents and molecular bounding of the matter. Measuring the T_2 could provide significant information on molecular structure.

As stated earlier, the ALE technique has been applied to analyze FID spectra. ALE operation (Fig. 3) can be briefly described as follows. A fixed delay Δ is inserted in the desired input, which is drawn directly from the primary input. The delay components, with sufficient length, cause a simple phase shift between desired the signal and the input signal. Based on the least-mean-square (LMS) algorithm, the adaptive filter uses error signal to form a transfer function so that the unwanted signals cancel each other at the summing junction.

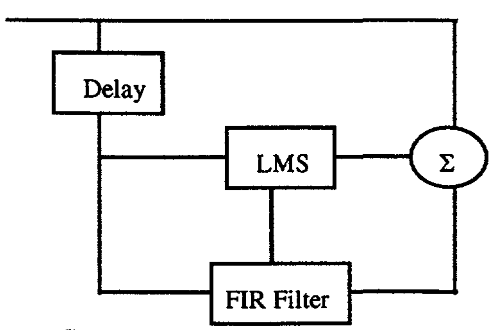

Fig. 3 Adaptive line enhancer(ALE)

The LMS algorithm for the adaptive line enhancer can be shown as follows

$$w_{i+1}(n) = w_i(n) + 2\mu\left[x(i)x(i-\Delta-n) - x(i-\Delta-n)\sum_{k=0}^{k-1} x(i-\Delta-k)w_i(k)\right] \qquad n = 0,1,..,k-1 \quad (2)$$

where $w_i(n)$ represents the weights of the filter and k is the number of weights. The parameter μ is a constant that controls the stability and rate of convergence. If eq. 2 is stable, then w_i converges to the solution of the Wiener-Hopf maxtrix equation [ ]. Therefore,

$$\lim_{i\to\infty} E[w_i(k)] = w^0(k) \qquad (3)$$

With the Wiener-Hopf matrix solution being

$$R * w^0 = P \qquad (4)$$

where $R = \Phi(k) = E(x(i)*x(i+k))$ is the autocorrelation matrix and P is defined as a column vector with elements $\Phi(k+\Delta)$.

The mean square error can be shown by covariance matrix of the weight vector as []

$$\lim_{i\to\infty} \mathrm{cov}[w_i - w^0] = \mu\xi_{\min} \qquad (5)$$

$$\xi_{\min} = \Phi(0) - \sum_{n=0}^{k-1} w^0 * \Phi(n+\Delta) \qquad (6)$$

equation 6 reveals that the minimum value of ξ depends on the power or energy of the primary signal on the optimal weight vector as well as on autocorrelation of input signal.

Design Considerations and Simulation Results

The underlying principles in construction of an NMR spectrometer are briefly described below. The basis of any NMR system is the pulse controller that is used to measure the frequency of a nuclear resonance with sufficient accuracy. In principle, NMR spectroscopy involves generation of two RF pulses. The architecture in Fig. 4

shows this operation. The system consist of four blocks of first-in/first-out (FIFO) memory where the wave and phase information is stored.

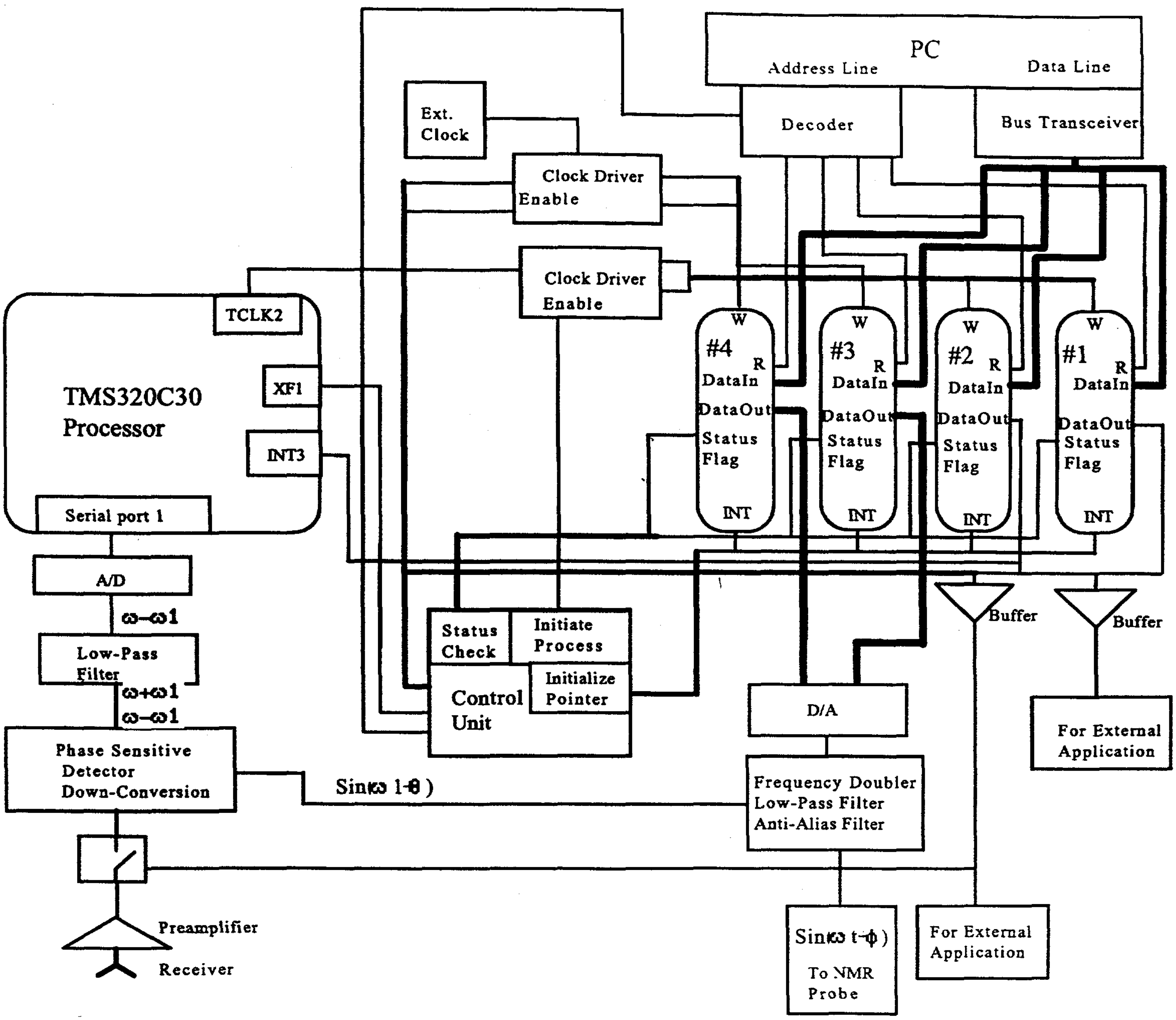

Fig. 4. A Block diagram of the NMR Controller

Memory blocks 1 and 2 are assigned to produce two pulses with sufficient delay. Parameters such as period, delay, and width of the pulse can be adjusted to be directly proportional to the frequency of the timer clock TCLK on the TMS320C30.

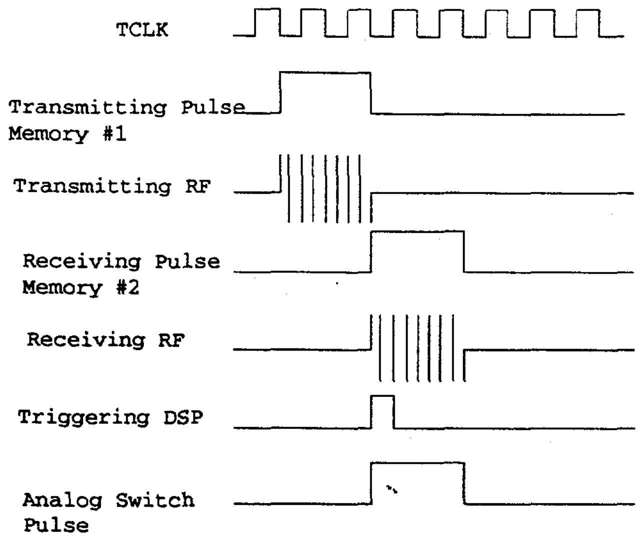

Fig 5. Timing diagram of NMR controller.

As shown in Fig. 5, the first pulse initiates a gated sinusoid by allowing Memory #3 to flash its data to the A/D chip. The end of the pulse is denoted by a status flag. Frequency of the waveform is chosen to be equivalent to the Larmer frequency (ω) of the nuclei. Figure 5 also shows the timing relationship between the receiving pulse and the various components within the circuitry. In general, there are three operations that accrue simultaneously:

1- A gated sinusoid is sent to an external mixer for down conversion of the output signal. Because the FID is oscillating in high-frequency the DSP can not digitally record the signal.

2- The external analog switch is enabled to transfer the NMR signal to the mixer.

3- The DSP is triggered by an external interrupt pin. This permits the DSP to start collecting data and executes the ALE procedure that distinguishes the desired signal from the composite signal.

To start a new cycle, the C30 processer uses an external flag (XF1) to initialize FIFO memory. When XF1 is set to zero, the stack pointer is directed to the top of the stack and the clock drivers are enabled.

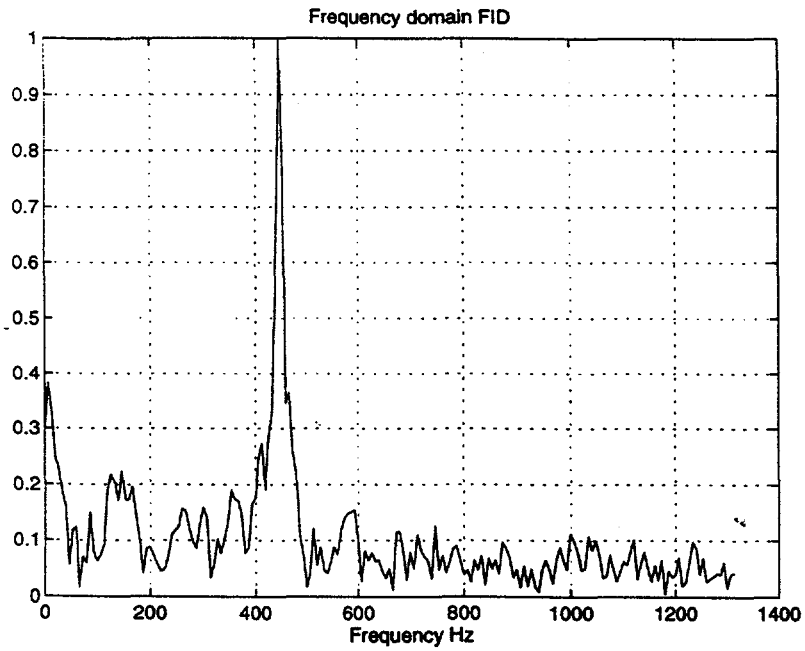

Fig. 6. Spectrum of composite signal

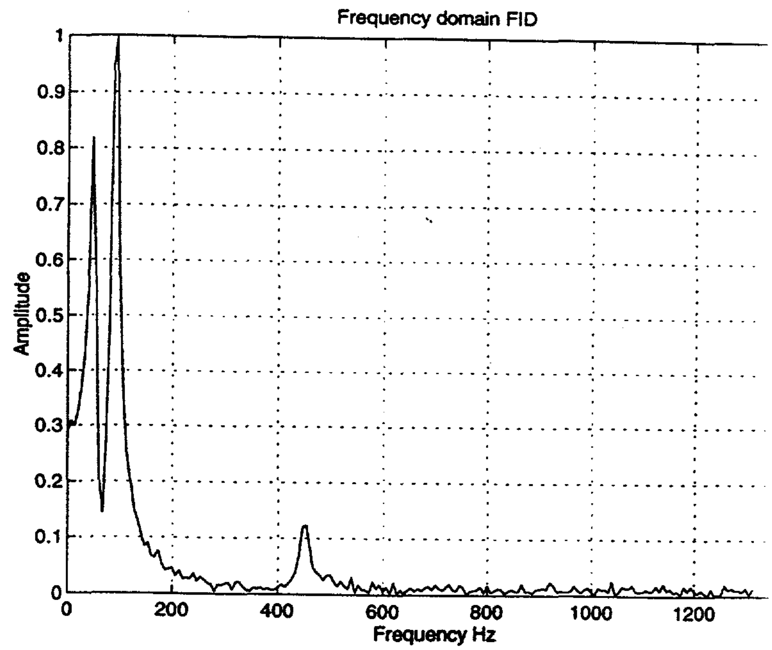

Fig. 7. Spectrum of the desired signal, after passing through ALE Output from ALE

When FID data are recorded by the DSP, the ALE routine is implemented to identify the desired signal. A computer simulation was carried out to demonstrate the detection of water in a composite spectra by applying the ALE procedure. Data ware collected from a series of off-line laboratory experiments. The FID spectrum of the input signal is shown in Fig 5, and the final result is shown in Fig. 6. It is clear that the system removed the unwanted background and kept the desired signal at 450 Hz.

Conclusion

In this paper, development of an on-line controller based on the TMS320C30 processor has been described for measuring of nuclear resonance using an adaptive line enhancer (ALE) method. This approach does not require an external reference signal for detection and observation of the desired signal. As shown in Fig. 6, an ALE filter can also be used to detect a weak signal in the presence of strong components and background noise. such systems have a high potential for on-line monitoring applications and may contribute greatly to improved process control. The main objective of this work has been to improve the NMR technique for applicability with reasonable accuracy as an on-line method rather than as a laboratory standard.

References

[1] Chen, C. and D.I. Hoult, "Biomedical Magnetic Resonance Technology", Adam Hilger, Inc., New York, NY. 1984.

[2] Fukushima, E. and S.B. Roeder, "Experimental Pulse NMR a Nuts and Bolts Approach", Addison-Wesley, Inc., Massachusetts. 1981.

[3] Haykin, S. "Adaptive Filter Theory", Prentice-Hall, Inc., Englewood Cliffs, N.J. 1991.

[4] Shaw, D. "Fourier Transform NMR. Spectroscopy", Elsevier, Inc., New York, NY. 1984.

[5] Texas Instruments, Inc. "TMS320C3x User's Guide", User's Manual, 1994.

[6] Windrow, B. and S.D. Stearns, "Adaptive Signal Processing", Prentice-Hall, Inc., Englewood Cliffs, N.J. 1985.

[7] Widrow, B. "Adaptive Noise Cancelling: Principles and Applications," Proc. IEEE, vol. 63, pp. 1692-1716, Dec. 1975.

[8] Widrow, B. "Adaptive Filter" in Aspects of Network and System Theory, .ed. R. E. Kalman and N. DeClaris, Holt, Rinehart and Winston, New York. 1971.

[9] Zeidler, J. R. et al. " Adaptive enhancement of Multiple Sinusoids in Uncorrelated Noise", IEEE Trans. Acoust. Speech Signal Process, vol. ASSP-26, pp. 240, June 1978.