AN EFFICIENT DIGITAL PHASE SENSITIVE DETECTOR FOR USE IN ELECTRON SPIN RESONANCE SPECTROSCOPY

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ABSTRACT

A digital phase sensitive detector for a modified Bruker electron spin resonance (ESR) spectrometer, equipped with an Aspect 2000 minicomputer is described. Magnetic field modulation is derived from a clock in the computer, which makes it possible to perform the data acquisition fully synchronously with the modulation. The resulting high phase accuracy makes it possible to compress the data to a single modulation period before the Fourier transformation. Both the in-phase and the phase-quadrature signals (of the first or second harmonic) are recorded simultaneously. The system is so efficient that the data processing including the Fourier transformation is approximately 1000 times faster than a previously reported digital phase sensitive detector system for ESR (T. Watanabe et al., Appl. Spectroscopy 34, 456 (1980)).

INTRODUCTION

Phase sensitive detectors (PSD) have been used extensively and with good results in many types of spectroscopy. Until a few years ago the so-called in-phase recording was by far the most widely used detection mode. Today several non-linear techniques such as saturation transfer ESR[1], make use of the phase-quadrature signal. Other methods, such as the magnitude saturation transfer ESR[2] and magnetization hysteresis ESR[3,4], require a simultaneous observation of both the in-phase and the phase-quadrature signals. It seems to be a general trend also in other fields of spectroscopy to use both signals, or the magnitude and phase signals. Consequently, new commercially available lock-in-amplifiers often provide the possibility of observing these signals simultaneously.

It is possible to replace an analog PSD with a digital one, by performing a Fourier transformation (FT) of the time data[5-7]. Such methods have several advantages compared to an analog system, but they are often hampered with a poor signal-to-noise (S/N) ratio. Furthermore, the Fourier transformation requires considerable computer time, thus fast sweeps have been unattainable by these methods[5,6].

One reason for this inefficiency of the digital PSD system is the fact that the data acquisition is performed asynchronously with respect to the modulation (or the recorded) signal. (The system briefly described by Saniie and Luukkala[8] may be an exception for this.) The "time signal" is obtained over several (many) signal periods and the data Fourier transformed (or equivalent) in order to obtain the "frequency domain" signal with sufficient phase accuracy. This method can also results in a slight frequency error which will reduce the quality of the data.

In this report a fully synchronous system will be described. The time data can be compressed to one modulation (signal) period before the FT without loss of phase accuracy. Thus, the FT becomes very fast and the overall system very efficient. Only a few minor modifications of the original spectrometer system were required to obtain the digital PSD function.

SYSTEM DESCRIPTION

The digital PSD system is outlined in Fig. 1. The ESR spectrometer is a Bruker ER-200-D instrument, equipped with an Aspect 2000 minicomputer. The system takes advantage of the minicomputer's analog-to-digital converter unit (ADC) and associated clocks, which may be synchronized by the timing control circuity.

Modulation of the magnetic field is provided by the Aspect dwell clock which is programmed to run continuously at twice the modulation frequency. The pulsed output of this clock is converted to a symmetrical square wave (modulation clock) and then shaped to a sinus signal by the modulation filter and amplifier circuits of the ER 022 receiver.

The detected ESR signal is taken from the output of the ER 022 filter and amplifier section and fed to the 12 bit ADC, bypassing the analog PSD circuits.

The ADC can operate in various direct memory access modes which our system uses as follows; two registers are loaded with the starting address to a memory block and the number of points to be acquired. When the ADC receives a start command it waits for a trigger input after which each sample clock causes a new data acquisition and the result is added directly to memory. The memory address register is automatically incremented after each acquisition until a set number of points have been acquired. The ADC now waits for a new software initialization.

The modulation clock (dwell clock divided by two) is used as the trigger input, providing a modulation phase reference for the acquired data series. A combination of pulse clocks 1 and 2 is used for the sample clock. Both clocks are needed since they are designed to give a single pulse of programmable duration. By configuring clock 1 to start clock 2 at the end of its period, which in turn starts clock 1, a continous clock is obtained. All clocks are derived from the same 10 MHz oscillator and clock 1 is initially started by the modulation clock through the trigger input. To maintain synchronization the period of clock 1/clock 2 is chosen to give an integral number of samplings per modulation period, resulting in jitter-free data acquisition.

Fig. 2 is a diagram showing the few modifications required to implement the system. All the modifications are controlled by previously unused bits of one of the slow channel registers in the ER 144C Aspect interface. The computer program is designed to select either analog or digital PSD mode.

Two gates were placed in the ER 022 receiver. An analog gate (G5) bypasses the analog PSD and a digital gate (G4) selects internal or external modulation. The gates are controlled by the PSD mode signal from the slow channel registers. The 'dwell' external modulation clock is also taken from the ER 144C interface.

The remaining modifications were made to the ER 144C interface. Gate G3 selects either the address advance signal from the time base (normal operation) or the Aspect pulse clocks 1-2 as the sampling clock for the ADC. G2 (already present) selects either the pen up/down signal from the time base (normal operation) or the modulation clock for the ADC trigger input. This gate was intended for an external trigger (T2), but the modulation clock is now internally connected in its place. A flip flop converts the pulsed dwell clock to a square wave (modulation clock) at half the frequency. At 100 kHz modulation it is necessary to obtain a synchronization period twice the modulation period (see below).

An additional flip flop is used to produce a trigger signal at half the modulation frequency. Selection of this trigger signal is also computer controlled (not shown in Fig. 2).

One of the slow channel registers provides control of the ER001 time base, enabling the program to reset and start the magnetic field sweep. The external clock input to the time base is normally the dwell clock. In the present system a gate (G1) is inserted which selects a "soft clock" to advance the time base. This "soft clock" is a single bit in the slow channel register which can be toggled by the program. It is thus possible to step through the magnetic field at any desired rate and step size, holding the field constant during data acquisition.

Since the present system uses the amplifiers and filters of the ER 022 signal channel, the choice of modulation frequencies is limited. The "dwell"/modulation clock, which can be set to within 2 μsec, has a negligible difference (10^{-3}) from the clocks used internally in the analog PSD mode. Thus, there is no detectable difference in the modulation amplitude for the two configurations.

THE FOURIER TRANSFORMATION

For a digital PSD the Fourier transformation is an essential step. We will therefore discuss this in detail before proceeding with the program description.

The Fourier transform of a time series $x(n)$ where $n = 0,1,\ldots, M-1$, is given by:

$$I(k) = \sum_{n=0}^{M-1} x(n) \cos(2\pi kn/M) \quad k = 0,1,\text{---}, M-1 \qquad [1]$$

Eq. 1 yields the real part of the FT, while the imaginary part is obtained by replacing cosine with sine in the expression above. These expressions correspond to the in-phase and phase-quadrature signals, respectively. For an asynchronous system the optimum k value corresponding to the signal frequency (modulation frequency) is not known in advance. In that case I(k) is often calculated for a complete set of frequencies (or k-values) using a fast Fourier transform algorithm, and M is usually a large number. Even though the fast Fourier transform is very efficient, it has to be repeated for every point in the spectrum. Thus, most of the time required for ESR recordings with the previously reported systems[5,6], was used for the FT.

For a fully synchronous system the exact k value in Eq. 1 that corresponds to the signal of interest is known in advance, and the signal I(k) needs only to be calculated for this particular k value. Furthermore, let M be chosen so that $k \cdot N = M$, where k is the number of complete signal periods, and N is the number of points per period. Then simple mathematical manipulation, using the periodicity of the sine and cosine, enables Eq. 1 to be rewritten in the following form:

$$I = \sum_{n=o}^{N-1} \left(\sum_{m=o}^{k-1} x(n + m \cdot N) \right) \cos(2\pi n/N) \qquad [2]$$

In a synchronous system the signal component of x is identical for all m values. The sum

$$X(n) = \sum_{m=0}^{k-1} x(n + m \cdot N) \qquad [3]$$

will therefore be proportional to the signal component of x while the noise component becomes proportionally smaller (averages out) with increasing k.

The number of samplings, N, per modulation period is usually a small number, so that the number of multiplications involved in calculating I according to Eq. 2 is greatly reduced compared to that for Eq. 1.

N should be an even number in order to supress any constant term in x. Furthermore, it can be shown that all the first N/2 harmonics will be supressed completely when Eq. 2 is used. For most ESR applications, N may be as low as 4 or 6. (We use N = 20 for 12.5 kHz detection with no great loss of efficiency.)

Due to phase shifts several places in the electronics the sampled signal is phase shifted with respect to the modulation signal that initiates the time series acquisition. To correct for this the following expression for the FT is used

$$I = \sum_{n=o}^{N-1} X(n) \cos (2\pi\, n/N + \phi) \qquad [4]$$

Even though Eq. 4 is derived for first harmonic detection it can be used for second harmonic detection as well. In this case, however, k in Eq. 3 is the number of complete second harmonic signal periods, N is the number of points per second harmonic period, and k must be an even number to supress the first harmonic signal.

For 100 kHz signal detection special procedures must be followed. The shortest sampling period with the present ADC is 4 μsec, thus only two and a half samplings can be carried out during a modulation period of 10 μsec (assuming first harmonic detection). We use a synchronization period equal to twice the modulation period and can obtain five samples in this period (at 0, $4\pi/5$, $8\pi/5$, $12\pi/5$, and $16\pi/5$). Because of the periodicity in the sine and cosine this is equivalent to sampling at the phases 0, $2\pi/5$, $4\pi/5$, $6\pi/5$, and $8\pi/5$, giving five samplings per modulation (detection) period. With this synchronous system one can in fact obtain an effective sampling frequency of 500 kHz with a system that actually function at 250 kHz ! In this case Eq. 4 is replaced with:

$$I = \sum_{n=0}^{N-1} X(n) \cos(4\pi n/N + \phi) \qquad [5]$$

where X(n) is calculated from Eq. 3, but N is now the number of points per synchronization period (5 for 100 kHz detection). When Eq. 5 is used with N = 5 (odd number), there will not be a complete mathematical suppression of the second harmonic signal at 200 kHz (the fourth harmonic for 50 kHz modulation). This does not seem to be a serious problem since the bandpass filter of ER 022 reduces these harmonics quite effectively. Possible problems in this respect will be investigated in near future.

PROGRAM DESCRIPTION

The computer program used for the digital PSD is outlined in Fig. 3 and operates as follows: The sine and cosine terms in Eq. 4 are calculated to make a list that is used in the FT step. The pulse clocks are started, and the gates in the interface and receiver units are set to allow digital use of the system. From now on the modulation is controlled by the Aspect 'dwell clock' which runs continously. The magnetic field sweep is reset at this time. The time series array is then zeroed, and the time series data, x(n) in Eq. 4, are collected using the ADC. This series is compressed to one modulation (or synchronization) period according to Eq. 3, and the two Fourier transformations corresponding to Eq. 4 or 5 are carried out.

The results are stored in the spectra arrays (in-phase and phase-quadrature spectra), and one of them displayed using the Bruker Graphic Display Processor. The magnetic field is then stepped to a new value and kept constant during the next time series accumulation. This procedure is continued until the sweep is complete. At this stage the data can be smoothed by a suitable digital filter, and the final spectra, along with user information, are stored on file (hard disk) for future processing.

In the construction of the sine and cosine lists for the Fourier transform, the sine table of the Aspect 2000 computer is used. This table consist of 512 numbers describing a 90 degree interval with 24 bits accuracy in a fractional number representation (as opposed to floating point). This representation is continued in our sine and cosine lists in order to speed up the multiplication step at the FT stage. Only 22 bits accuracy is used, however, in order to include even the sine = 1 case. The phase shift ϕ of Eq. 4 is obtained by introducing an effective cyclic shift in the Aspect sine value table. Thus, ESR spectra can be recorded for any value of ϕ in steps of about one sixth of a degree. The ϕ value is chosen *prior* to recording each spectrum, using for example the ϕ value that gives the *minimum* phase-quadrature signal.

The analog-to-digital converter of the Aspect computer is used in a direct memory access mode where the data are automatically added to a memory block. In principle, this block could be as small as N registers long, thus only using the ADC for one modulation period each time. In this way all the summation of Eq. 3 would be performed automatically during the data acquisition. However, such a procedure would yield a considerable dead time since the ADC must wait for the start of the next modulation period to maintain phase synchronization, especially for 12.5 kHz detection. Therefore, the most efficient procedure is one where the summation of Eq. 3 is performed partly during and partly after the data acquisition. For 12.5 kHz modulation, for example, if 400 modulation periods are sampled (k = 400 in Eq. 3) the ADC memory block can be 20 modulation periods (20·N points) long and the ADC started 20 times.

PERFORMANCE AND POTENTIALS

In order to evaluate the quality of the present digital PSD some central features of the system should be discussed.

Sweep time

The time needed to record a complete ESR spectrum (the sweep time), can in the present system be varied in two ways. First, the total sampling time for each fixed magnetic field value can be varied from a minimum of one modulation period to infinity (with minor modifications of the program to avoid overflow). Secondly, the number of points per sweep can be chosen freely, but is limited by the resolution of the time base (8192 points). For most applications it will suffice to use 1024 points resolution in the magnetic field sweep and accumulate about 8000 samples (time series data) per magnetic field value with a 250 kHz sampling rate. Such a choice results in a total sweep time of 41 sec for 12.5 kHz detection (39 sec for 100 kHz detection). The total sampling time is about 33 sec and the mathematical manipulations, including the FT, the display of current data, and the control of the magnetic field takes 8 (6) sec. Thus, the fastest sweep that can be carried out for a 1024 point ESR spectrum is actually limited to about 10 sec (due to the Hall controller and not to the program), while there is no limit for how slow a sweep can be.

Filters

To improve the quality of the data, analog lock-in-amplifiers use low-pass filters after the PSD to suppress high frequency noise. The filter constant (cut-off value) is usually chosen by "rule of thumb". However, this kind of filtering is asymmetrical since only the preceding input signal is taken into account to determine the output from the filter. Because of this, an apparent magnetic field shift of the ESR resonance will result which in turn causes problems for example in g-value measurements[9].

In the digital PSD mode a symmetrical digital filter is used which prevents a shift of the resonance. Furthermore, since the filter can be chosen subsequent to an examination of the untreated spectrum , an optimal cut-off value can be chosen. Blackman finite impulse response filters with different window sizes have been used in this work since this kind of filter attenuates the higher frequencies very efficiently[10]. Other kinds of digital filters are now being investigated to obtain the best possible signal-to-noise ratios for typical ESR spectra. The time needed for filtering with 41 weights (k = 43 in reference 10) on a 1024 point spectrum is 1.5 sec. Lower k values are usually used resulting in even shorter times.

In order to compare signal-to-noise ratios for analog and digital PSD systems a correspondence between analog and digital filters must be established. It is not straightforward to compare these filters since the criteria for such a comparison is not self-evident. Fig. 4 shows the ESR spectrum we used for comparison of the filter constants for analog and digital PSD. The amplitudes of one of the narrow lines (SL) and the wide line (Mn) were measured for a set of filters (constant sweep time of 50 sec for both systems). The efficiency of the filters were increased to introduce changes in the amplitude ratio SL/Mn. An analog and a digital filter yielding the same change in the SL/Mn ratio were then defined equivalent for ESR purposes. According to this definition a k = 33 Blackman filter for a 1024 point spectrum (digital PSD), for example, is equivalent with a filter constant of 0.5 sec for a 50 sec sweep (analog PSD).

Signal-to-noise ratio

In order to evaluate the S/N ratio obtaied by the digital PSD it is natural to compare it with the analog system. Such a comparison will, however, be influenced by the actual value of the S/N ratio of the recorded signal. For a good ESR signal (high S/N ratio) the time domain signal to the ADC will be a clean (pure) sine-wave. The maximum signal will span most of the ADC input voltage range. The numeric data of the final spectra will then consist of numbers with approximately 20 bit effective resolution as a result of the summation steps in Eqs. 3 and 4. If an analog PSD is used, and the resulting signal put into the ADC, the final spectrum would be represented by numbers with only 12 bit effective resolution. The practical consequencies of this difference is demonstrated in Fig. 5. A magnetization hysteresis ESR spectrum using analog PSD data is given in a, whereas the same spectrum, using digital PSD data, is presented in b. As can be seen in the diagram the digital PSD results in a significantly reduced noise level. Equivalent filters were used and the digital PSD system required less than half the time needed by the analog PSD.

For a poor ESR signal (low S/N ratio) the situation is somewhat different. In order to avoid serious clipping of the time domain signal (at the ADC), the amplification must be reduced in digital PSD compared to that for analog PSD. In this case the limited resolution of the ADC will affect the digital system to a greater extent than the analog one. In spite of this, a 50% weak pitch sample seems to give identical S/N ratio (within 10-20%) for the digital and the analog systems (when equivalent filters and 50 sec sweep time is used).

CONCLUSION

The digital PSD system described here is the second one for ESR applications reported in the literature, the other being the system described by Watanabe and coworkers[6,5]. Several improvements should therefore be mentioned. In Watanabe's system the data processing including the FT for every point in the spectrum required approximately 5 sec[6] (8 sec in reference 5), whereas the present system requires only 6-8 msec. Furthermore, only 21 sec out of a total sweep time of 40 min (500 points) were used for data acquisition in Watanabe's system, whereas the present system uses for example 33 sec out of 41 (38) sec (1024 points), respectively. These relations will obviously effect the S/N ratio obtained by the two systems. Watanabe (personal communication) assumes that the S/N ratio in their system is poor compared to an analog PSD system. The present digital PSD system, has, on the other hand, approximately the same S/N ratio as the analog PSD. Furthermore, we would like to emphasize the point that in experiments where both the in-phase and the phase-quadrature signals are used simultaneously, the digital system is the superior one. Of other major differences can be mentioned that the present digital PSD system is free from jittering which means that this source of phase inaccuracy is completely avoided. Furthermore, the present system controls the magnetic field sweep so that the field is constant during data acquisition.

In the system presented by Watanabe et al.[6] both first and second harmonic signals can be recorded simultaneously. In the present system the mode of observation must be chosen before the sweep is started. It is of course simple to modify the present system to record both harmonics simultaneously. We see no point in doing this, however, since it would require that the filter before the ADC had to be bypassed with corresponding loss of S/N and dynamic reserve.

Some of the advantages of a digital PSD system should be mentioned. When the in-phase and phase-quadrature signals are combined as for example in a magnitude or phase spectrum, it is essential that there is no shift in one spectrum relative to the other. Previous works[3,4] required a good stability of the spectrometer system since the two spectra were recorded one after the other. In digital PSD systems, both signals are recorded simultaneously and all errors due to drift are eliminated. Another point is that the in-phase and phase-quadrature spectra obtained by digital PSD are separated by exactly 90 degree phase difference, whereas analog systems have to be calibrated to yield this phase difference.

Recording of in-phase and phase-quadrature spectra simultaneously yields opportunities to construct signals at any desirable phase subsequent to spectra recording. Such a construction may be problematic if analog PSD is used since these spectra may have a DC offset (baseline shift). The same problem does not exist with digital PSD systems.

In conclusion the present digital PSD should be very well suited for all the non-linear ESR techniques discussed above, namely saturation transfer, magnitude saturation transfer, and magnetization hysteresis ESR. Furthermore, the principles of synchronous modulation and data acquisition should be applicable in other fields of spectroscopy as well.

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REFERENCES

1. D.D. Thomas, L.R. Dalton, and J.S. Hyde, J. Chem. Phys. 65, 3006 (1976).

2. M.A. Hemminga, and P.A. deJager, J. Magn. Reson. 43, 324 (1981).

3. A.I. Vistnes, Biophys. J. 43, 31 (1983).

4. A.I. Vistnes, and L.R. Dalton, J. Magn. Reson. 54, 78 (1983).

5. T. Sasaki, Y. Kanaoka, T. Watanabe, and S. Fujiwara, J. Magn. Reson. 38, 385 (1980).

6. T. Watanabe, T. Sasaki, K. Sawatari, and S. Fujiwara, Appl. Spectroscopy 34, 456 (1980).

7. G.J. Gerritsma, W.J. van Weezep, J.A. Overweg, and J. Flokstra, J. Phys. E: Sci. Instrum. 16, 270 (1983).

8. J. Saniie, and M. Luukkala, J. Phys. E: Sci. Instrum. 16, 606 (1983).

9. D.I. Wormald, E. Sagstuen, and A.I. Vistnes, Rev. Sci. Instrum. 53, 1145 (1982).

10. A.V. Oppenheim, R.W. Schafer, Digital Signal Processing (Prentice-Hall, Englewood Cliffs, N.J., 1975).

FIGURE LEGENDS

Fig. 1. Block diagram showing the timing of the modulation and the ADC sampling. A common 10 MHz clock and reset circuits ensure synchronization.

Fig. 2. Block diagram describing the few modifications of the original spectrometer system necessary for digital PSD use.

Fig. 3. Flow chart for the computer program performing the digital PSD.

Fig. 4. The ESR spectrum used for comparing analog and digital filtering of the spectrum. The sample consists of an aqueous solution of a spin label (tempo-choline-chloride) and Mn^{++}. The Mn^{++} spectrum is exchange broadened, and only a part of the two midfield Mn^{++} lines are included in this sweep (100 gauss). The digital PSD was used for this recording.

Fig. 5. Magnetization hysteresis ESR spectra obtained by analog (a) and digital (b) PSD. The sample is a tiny NMP-TCNQ crystal[4]. The modulation frequency and amplitude were 12.5 kHz and 40 mG, respectively. 2 mW incident microwave power to a standard X band rectangular cavity was used. The total time needed for spectra recordings were approximately 120 and 40 sec for the analog and digital signals, respectively.

<u>Figure 1.</u>

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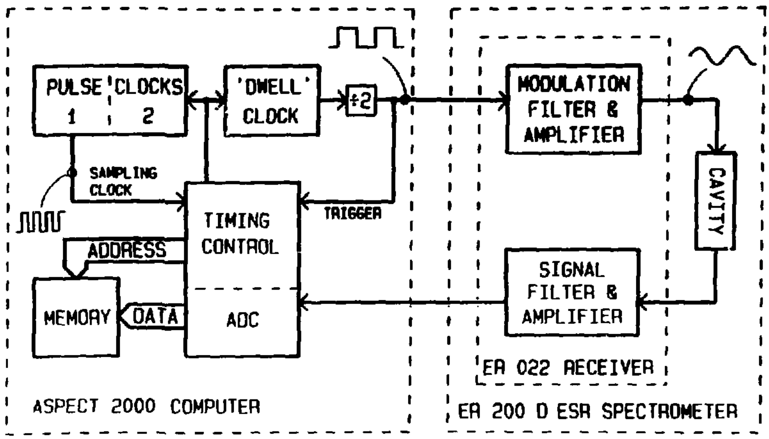

Figure 2.

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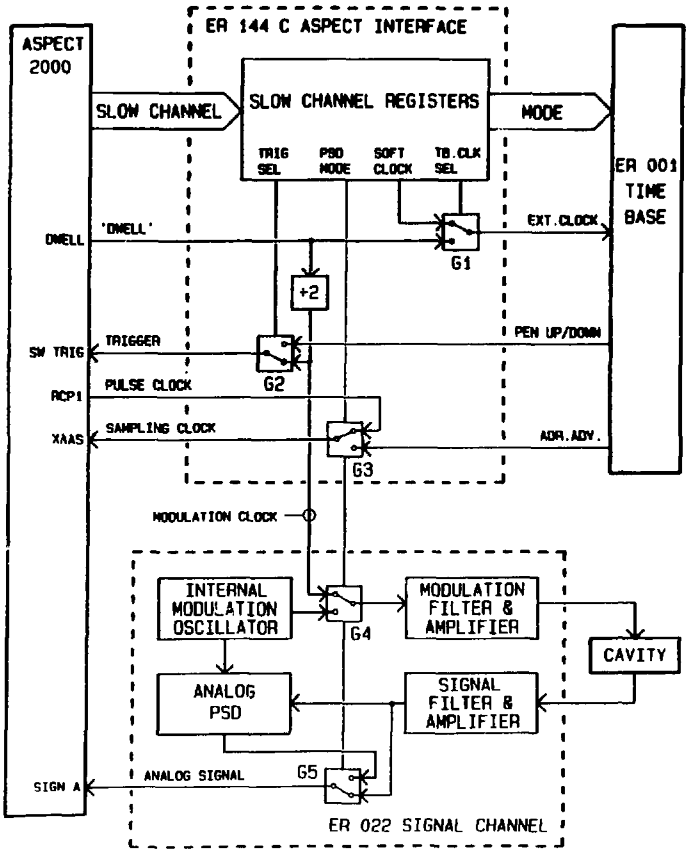

Figure 3.

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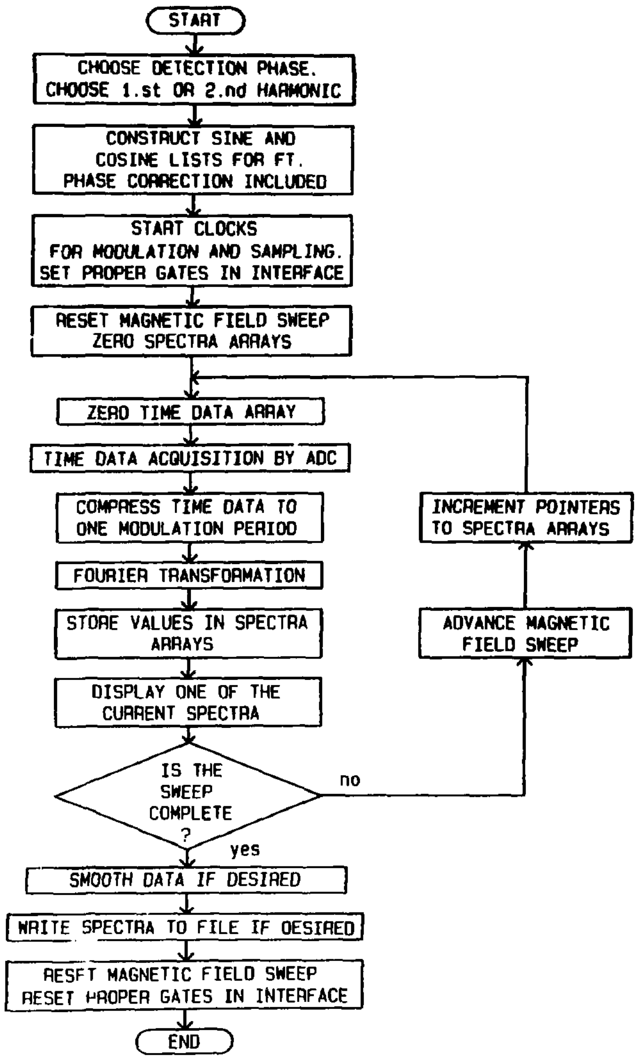

Figure 4.
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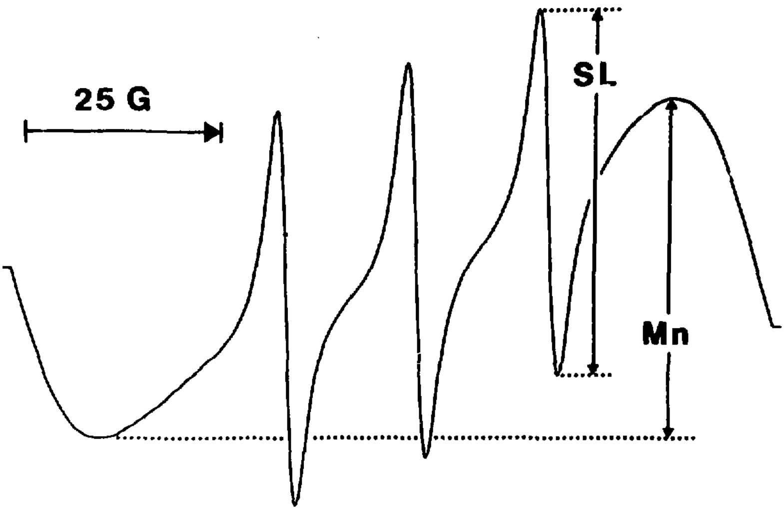

Figure 5.
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