REVIEW ARTICLE

Automation and control in high power pulsed NMR

A Geiger and M Holz
Institut für Physikalische Chemie und Elektrochemie der
Universität Karlsruhe Kaiserstrasse 12, D-7500 Karlsruhe,
West Germany

Abstract The article reviews developments in control and
automation of conventional high power pulsed NMR
spectrometers. A short introduction to the physical
background and the methods is given. Automation and
control of the various components of a pulsed NMR
spectrometer are then illustrated and problems are discussed.
Following this, concepts of spectrometer system automation
are treated, using examples of home made, as well as
commercial equipment. Another section is devoted to the
automation of a pulsed NMR lab comprising several NMR
spectrometers. Finally the application of pulsed NMR
spectroscopy in industrial processing is discussed.

1 Introduction

At the Chicago Meeting of the American Physical Society in
November 1949 E L Hahn reported that he had discovered a
'new technique for obtaining nuclear magnetic resonance after
the applied RF field is turned off'. Bloch (1946) had already
pointed out that one can expect to obtain a nuclear induction
signal in the absence of an RF field after having perturbed the
nuclear spins by a short intensive RF pulse having the resonance
frequency of $\omega_0 = \gamma H_0$ (γ being the gyromagnetic ratio of the
nuclei and H_0 the strength of the external magnetic field). In
his famous paper Hahn (1950) then described in detail the
new 'spin–echo technique', theoretically as well as experi-
mentally, and this may be regarded as the beginning of
'pulsed NMR'. This new method differs from the commonly
used continuous wave (CW) NMR spectroscopy in the way it
irradiates and observes NMR signals.

The basic principle of pulsed NMR is easy to understand.
Just as a tuning fork oscillates after a short blow with a
hammer, the nuclear spin system oscillates freely for a certain
time after a short RF pulse. The signal induced in a receiver coil
by the resonant spins is called the 'free induction decay'
(FID) and is observed as a function of time ($f(t)$). Thus pulsed
NMR is performed in the 'time domain', as opposed to CW NMR
in the 'frequency domain' where the signal amplitude is
measured as a function of frequency.

Measurements as a function of time are especially suitable
for the determination of relaxation times and diffusion
coefficients, thus the pulsed NMR spectrometers in the 1950s
and 1960s were most frequently used by physicists and
physical chemists to study these quantities. Typical NMR
spectra for the structural analysis in chemistry were measured
with CW spectrometers. For the measurement of relaxation
times in one-line systems, as for example protons in H_2O, no
high magnetic field homogeneity is necessary and therefore the
pulsed spectrometers could be equipped with relatively simple
magnets and magnet power supplies. Moreover, due to the
'spin-echo effect', inhomogeneity effects could be eliminated
and it was even possible to determine with those simple
magnets the natural line widths via T_2 measurements. As may
be seen below the basic concept of a pulsed NMR spectrometer
is not too complicated and therefore many papers appeared
where 'home-built' pulsed spectrometers were used and
described, a tendency which, compared to CW spectrometers,
is remarkable, although it has become weaker in recent years.
From about 1960 simple pulsed NMR spectrometers could be
obtained from commercial manufacturers such as Bruker and,
for a period of time, Magnion (Ventron) and NMR Specialities.

During the second half of the 1960s two independent
developments brought an unexpected advance in pulsed NMR
spectroscopy. First Ernst and Anderson (1966) demonstrated
that the observation of NMR signals in the time domain
followed by a Fourier transformation (FT) of the signals in a
computer has tremendous advantage compared with ordinary
CW spectroscopy. This led to the development of high resolu-
tion FT spectrometers which are today to be found in almost
all chemical research laboratories. (The advances in this field
have been reviewed in this journal by Shaw (1974) and will not
be the subject of the present article.) Today spectrometers of
this type are produced commercially e.g. by Bruker, Cameca,
Jeol, Nicolet, Perkin Elmer and Varian. The second develop-
ment was initiated by J S Waugh and co-workers, who deve-
loped a wealth of techniques based on multiple pulse sequences
which overcame the natural line broadening mechanisms in
solids, thus allowing high resolution spectroscopy in solids.
These 'line narrowing' experiments were reviewed in an
excellent monograph by Mehring (1976). Today we may
classify pulsed spectrometers as CW, FT and 'high power'. The
supplement 'high-power' indicates that in simple pulsed NMR
RF pulses with relatively high intensity are applied, whereas in
FT spectroscopy weaker RF field strengths are usually used. In
this sense the subjects of the present article are the 'high
power' pulsed spectrometers.

Hahn in his first experiments applied two repetitive RF
pulses of equal amplitude and duration but varying distance.
In principle one can vary five quantities, namely the *frequency*,
amplitude, *phase*, *duration*, and *distance* of the RF pulses. Indeed,
in the last 30 years, a large number of variations on the original
experiment have been developed, differing in the above five
quantities, aiming to measure various quantities characterising
the microscopic state of matter. Furthermore, the required
number of measurements has increased drastically, because

for special questions long measuring series have had to be performed e.g. with different nuclei, varying concentrations, isotopic composition, temperature, pressure, frequency etc. A further increase in the time consumed stems from the need to time average weak signals when less sensitive nuclei, low concentrations of molecular and/or isotopic species have to be observed. Thus there are many reasons for automating pulsed NMR experiments, the main functions of such an automated system being:

(i) Generation of complicated pulse sequences.

(ii) Acquisition, time averaging and evaluation of signals.

(iii) Control and variation of 'internal' parameters like frequency, phase, probe damping etc.

(iv) Control and variation of 'external' parameters like magnetic field or temperature.

The main advantages of control and automation are reduction of the time required, the possibility of performing complex experiments, and a substantial improvement in the precision of the measurements. This precision increase is caused essentially by the following facts: time averaging leads to a signal-to-noise ratio enhancement, calculation facilities allow a more accurate evaluation of the signals and the automatic control of parameter setting results in increased accuracy and reproducibility of parameter setting and thus of experimental data. Moreover, the computer control allows the automatic optimisation of parameters with higher precision than by manual operation. This was shown in the case of pulse length and detector phase, as described later.

2 Fundamental quantities to be measured

The most important quantities measured with the 'classical' pulsed spectrometer were the relaxation times T_1 and T_2 and the self-diffusion coefficient D. T_1 is the 'spin-lattice' or 'longitudinal' relaxation time, which characterises the first order relaxation process by which the nuclear spin system returns to thermal equilibrium after a disturbance. T_2 is the 'spin-spin' or 'transversal' relaxation time and it is related to the half power width of a Lorentzian line $\Delta\nu_{1/2}$ by the equation $T_2 = 1/(\pi\Delta\nu_{1/2})$. If, during the relaxation process, an RF field (H_1) is present the spins are locked along the H_1 axis and one can then measure a relaxation time $T_{1\rho}$, usually called 'T_1 in the rotating frame'. A good introduction to pulsed NMR methods and a theoretical background to the above mentioned quantities has been given by Farrar and Becker (1971). In recent years a further relaxation time has become important in solid state investigations, namely T_{1D}, the 'dipolar relaxation time', which can be measured by a simple pulse sequence as proposed by Jeener and Broekaert (1967). The 'line-narrowing' experiments on solids yield, after Fourier transformation, high resolution spectra of solids from which, for example, chemical shifts and coupling constants may be determined. Finally we mention some further interesting applications of frequency-variable pulsed NMR spectrometers. Due to the frequency variability and the possibility of Fourier transformation they have also been used as spectrometers for pure nuclear quadrupole resonance (NQR). The spin-echo technique also allows measurements in powdered metals and even in magnetically ordered materials, where extreme broad resonance lines may be studied by a frequency dependent measurement of the spin-echo amplitude from which the line shape is then obtained point by point (see e.g. Feldmann *et al* 1971).

2.1 *Some typical pulse sequences*

If a magnetic field H_1 which oscillates with the nuclear resonance frequency $\omega_0 = \gamma H_0$, acts on a nuclear spin (con-
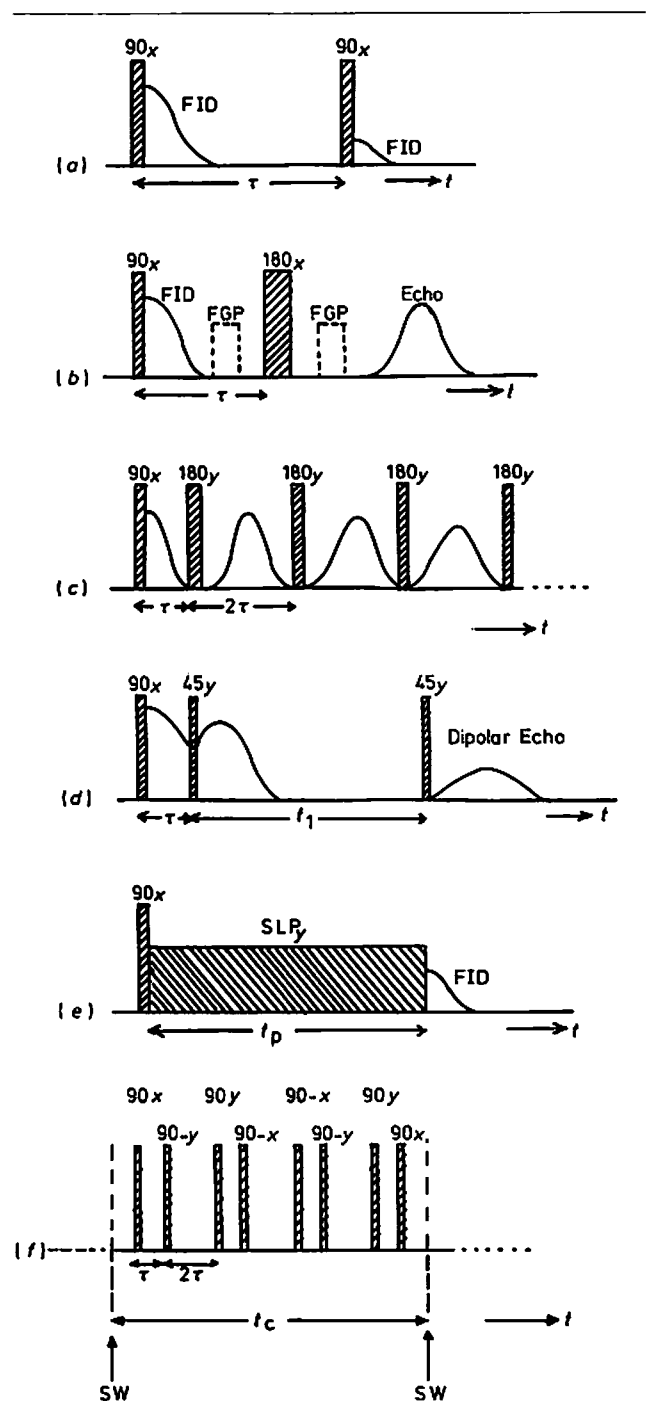

Figure 1 Some basic NMR pulse sequences:

(a) $(90°_x - \tau - 90°_x - T)_n$ for T_1 measurement. $T \approx 5 \cdot T_1$, repeated n times for various τ's. FID amplitude measured as $f(\tau)$. If the first $90°_x$ pulse is replaced by a $180°_x$ pulse one obtains the 'inversion recovery' sequence.

(b) $(90°_x - \tau - 180°_x - T)_n$ for T_2 and self-diffusion coefficient D measurement. Echo amplitude is measured as $f(\tau)$.

FGP: Field gradient pulses which are applied for D measurement. (c) Carr-Purcell-Gill-Meiboom sequence for T_2 measurement. $(90°_x - \tau - 180°_y - 2\tau - 180°_y \dots)$. Echo envelope is measured as $f(t)$. (d) $(90°_x - \tau - 45°_y - t_1 - 45°_y)_n$ for T_{1D} measurement. Dipolar echo is measured as $f(t_1)$.

(e) $(90_x - \text{SLP}_y)$ for $T_{1\rho}$ measurement. $\text{SLP}_y = \text{spin locking}$ pulse of variable duration t_p. FID is measured as $f(t_p)$.

(f) 8-pulse cycle ('MREV') for 'line narrowing' in solids. $\text{SW} = \text{sampling window}$, $t_c = \text{cycle time}$. The cycle during the experiment is permanently repeated and the signal at SW measured as $f(t)$.

nected with this spin is a magnetic dipole moment), it produces a precession of the spin around H_1. Therefore it is possible to rotate the nuclear magnetisation from the equilibrium direction (direction of the main field H_0, called z-direction) to any desired direction if one applies for a given time t_p (pulse duration), an RF pulse. These pulses are characterised by the tip angle α they produce, thus a '90° pulse' turns the magnetisation in the xy-plane, perpendicular to the main field and a '180° pulse' inverts the direction of the magnetisation. In general $\alpha = \gamma H_1 t_p$ is valid. The H_1 direction always lies in the xy-plane, but may be varied within this plane by appropriate RF phase adjustment. Thus a '90°$_x$ pulse' denotes a 90° pulse produced by a H_1 field in the x-direction. More details and in particular the description of the spin–echo formation and the measurement of diffusion coefficients are to be found in this journal in a review article by Singer (1978). Figure 1 shows some of the most important pulse sequences for the measurement of the above mentioned quantities.

3 The pulsed NMR spectrometer

3.1 Survey and block diagram

The block diagram of a typical pulsed NMR system, consisting of spectrometer and magnet is to be seen in figure 2. Main components of the spectrometer are: (i) Pulse programmer, which provides DC pulses, (ii) transmitter system with RF source, RF gates, phase shifters and power amplifier, (iii) probe, (iv) receiver system with pre-amplifier, main amplifier, phase sensitive or diode detector, audiofrequency amplifier, and (v) data acquisition and evaluation system. The function of the complete system is easy to understand: RF from a
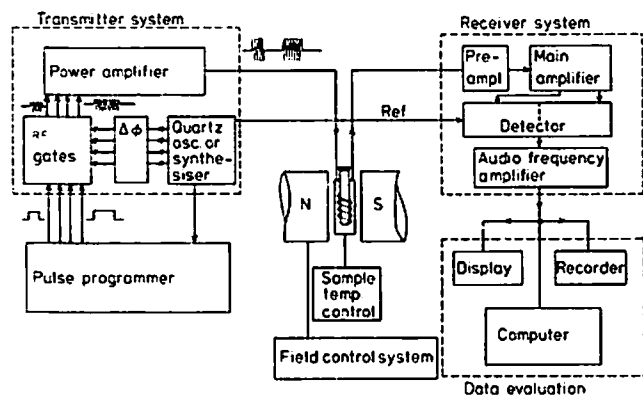

Figure 2 Block diagram of a pulsed NMR spectrometer. Detector can be either phase detector or diode.

continuously running quartz controlled oscillator is fed into different channels (typically four!) in order to be able to adjust different relative phases with a phase generation device. Each channel is then gated, so that only if a DC pulse from the pulse generator opens the gate of the channel may RF pass. Thus RF pulses differing in phase are produced, which, amplified in the power amplifier, are taken to the probe in the air gap of a magnet and act on the sample. The NMR signals, following the RF pulses and coming from the sample receiver coil, are then amplified and demodulated by diode or phase sensitive detection. The detected signal passes an audio-amplifier with adjustable bandwidth limitation and is then given to signal outputs which are normally connected with display units and a data acquisition system.

3.2 Components of the spectrometer and their automatic control

3.2.1 Field control
High resolution magnets for CW spectrometers are equipped with a highly sophisticated magnetic field control system, including current, flux and internal or external NMR stabilisation. Pulsed NMR may also require such a magnet system and then the magnetic field stabilisation is carried out in the same way. On the other hand most relaxation measurements may be performed in simpler and cheaper magnets with less homogeneity and stability. However, with weak signals, signal accumulation is necessary and then current and flux stabilisation are not sufficient. Therefore special NMR controller systems have been developed. For example Scheler and Anacker (1975) described a stabiliser with a stability of 10^{-7} where the control signal is generated by a 'time sharing' circuit with resonance at the first side band of a ^{2}H control signal. Kan *et al* (1978) performed the automatic field-frequency lock by observation of a ^{2}H FID following a short pulse, which is compared with an audiofrequency reference. The resulting error signal is used to control the field by conventional phase-lock techniques. Packer and Strike (1970) derived the error signal from the phase sensitive detector. An elegant principle which is particularly useful with low homogeneity magnets is applied in a commercial external NMR stabiliser, the Bruker B-SN 15. This instrument is a complete small pulse spectrometer which operates about 2000 Hz off-resonance, thus the FID produced with a high repetition rate is modulated with this beat frequency. Then the first modulation period is transformed to a gate pulse during which 100 ns clock pulses are counted. Field fluctuations alter the beat frequency and therefore the number of counted pulses. Deviations from the desired value are DA converted and applied as an error signal to control the field. Frequency deviations determined in exactly the same way were used by Geiger (1973) to correct the spectrometer frequency via the remote control of the synthesiser if the field changed. The ability to perform field-dependent (that is also frequency dependent) relaxation time measurements is of great importance. In order to have a range of stabilised fields Hawk *et al* (1974) developed a broad band 'time shared' NMR stabiliser using ^{7}Li or ^{1}H signals from a saturated LiCl solution in formamide for field corrections in the range 0·4–2·3 T. At low fields relaxation time measurements were extremely difficult due to the loss of signal intensity for these fields. Kimmich and Noack (1970) described in an interesting paper how to overcome the difficulties. They switch during the relaxation experiment from a high polarisation field to a low relaxation field and again to a high detection field. This is achieved by switching on directly after the RF pulse a second magnetic field which is opposite to the first (polarisation) field. The relaxation process is then going on in a weak field. Shortly before the second RF pulse (detection pulse) appears the opposite field is switched off and the signal is observed at high frequency. Von Goldammer and Kreysch (1978) applying this technique for ^{1}H used a polarisation (detection) field of 23·5 mT ($\triangleq$ 1 MHz) and relaxation fields down to 0·24 mT ($\triangleq$ 10 kHz).

With the introduction of superconducting magnets in the future microcomputers will surely also take control of field changing tasks and other solenoid status functions such as superconducting–normal transitions as, for example, described by Higgins *et al* (1978).

3.2.2 Pulse programmers
The central control unit of a pulsed spectrometer is the pulse programmer (PP) or pulse generator. This not only delivers gating pulse sequences to the trans-

mitter and receiver but also triggers the oscilloscope and the data acquisition device. This explains the fact that a large number of publications concern PPs of various stages of sophistication, using diverse ways to implement the demanded functions. The different types of PPs may be subdivided roughly into four categories:

1 single purpose hardware PPs,
2 hardware PPs with flexible hardware control,
3 hardware PPs with software control,
4 software pulse generators.

At present generators of the third type seem to be preferred because they accomplish simultaneously high accuracy and versatility. Because we are occupied here with problems of automation, single purpose pulse generators will not be treated (references may be found in the papers cited below, especially in Lind (1972), Franconi and Terenzi (1970) and Shenoy *et al* (1976)). First, hardware controlled PP will be considered. Digital as well as analogue techniques in diverse combinations have been used.

One strategy to get flexibility is to subdivide the device into several modules, which may then be interconnected in various ways, depending on the pulse program desired. Three types of basic modules are distinguished: The clock module, single pulse channel modules (or counter modules) and control modules. This concept was pursued by Lind (1972), Taylor *et al* (1974), Conway and Cotts (1977) and Adduci *et al* (1977). A simpler predecessor is described by Lalanne and Eletr (1970). Figure 3(*a*) shows in a schematic way the interconnection between these modules:
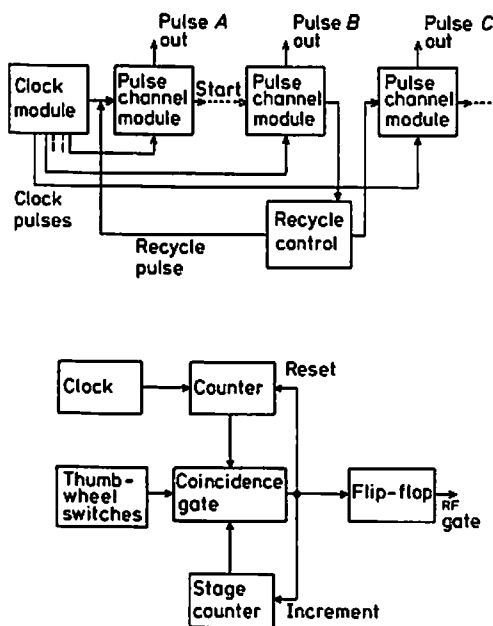

Figure 3 Schematic block diagrams of flexible hardware pulse generators.

The clock module has to start pulse sequences, to control the experiment's repetitition time and to provide the pulse channel modules with appropriate clock pulse trains by using a master clock (10–20 MHz) plus cascaded dividers.

Each pulse channel module generates a gating pulse for the RF transmitter followed by a delay time. Then a start pulse is sent to the next module. The gating pulse width may be generated by using monostable multivibrators or digitally by using high frequency counters. In that case these modules can

also be subdivided into two simple counter modules, one counting the pulse width, the other the delay time. This was done by Lind (1972). Digital pulse width generation has the advantage of reproducibility and easy remote setting. However, in some cases (mainly in solid state studies) the pulse widths have to be so short (H_1 is large) that a continuous adjustment is necessary. Care must be taken when using different clock frequencies for the different pulse channel modules. To avoid triggering errors the clock frequency used for higher stages must not be smaller than for previous stages. The recycling control module recycles the output of any channel to trigger a previous channel a preselected number of times. Thus repetitive pulse subgroups may be generated.

Another way of designing a versatile PP was shown by Ellett *et al* (1971) and Shenoy *et al* (1976). Shenoy *et al* use only one counter to produce all delays and pulse widths. Five sets of thumbwheel switches allow the preselection of three pulse widths and two delay times. The setting of these thumbwheel switches is compared with the actual counter reading by a coincidence circuit. The selection of the actual thumbwheel switch is done by a 'stage counter' according to the desired pulse program (figure 3(*b*)). Different pulse programs are produced by using different logic circuits to select the succession of thumbwheel switch reading. A comparable PP was described by Ellett *et al* (1971). These authors used plug-in cards to select different pulse programs.

Starting from these designs the ideas of software controlled PP can be grasped easily: thumbwheel switch setting is replaced by data stored in a memory, the selection logic under stage counter control is partly transformed to program instructions read under program counter control. The realisation of new pulse sequences is thus essentially reduced to a software problem. This kind of pulse programmer is organised like a central processor of a computer. As indicated, there are three main components: the memory unit, the control logic circuitry and the address counter. In the memory, data and instructions are stored, which are needed to produce pulse sequences. The control logic circuitry decodes bit patterns read from the memory and accordingly selects pulse and trigger channels, produces pulse widths and delay times etc. The address circuitry provides the address of the next memory word to be treated. Figure 4 gives a schematic diagram of a programmable pulse generator comparable to those described by Ellett *et al* (1971) and Matson (1975). Here pulse widths and also partly delay times are produced using manually set monoflops for continuous pulse width adjustment.

In recent designs pulse widths are also produced digitally, very high frequency counters (up to 100 MHz) enabling fine tuning. In this case the control words in the memory specify the logic levels of the output channels and the time during
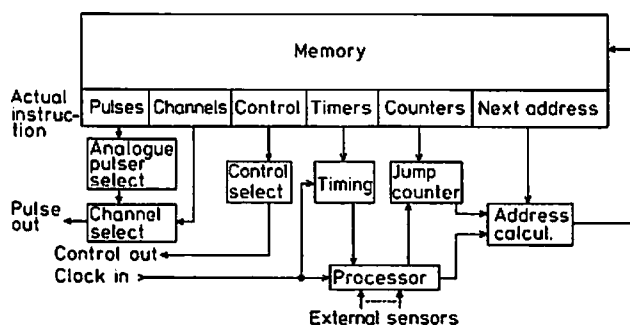

Figure 4 Schematic diagram of a programmable pulse generator.

which this state will be unchanged, before the next control word has to be executed, which specifies the new state of the output channels. This concept is also realised in commercially available timing simulators (TS) (Interface Technology Inc.). Karlicek and Lowe (1978) describe the use of this device in a broad band pulsed NMR spectrometer. Bruker also uses this method in its CXP-spectrometer series, but whereas the TS used by Karlicek *et al* allows only sequential execution of the memory contents the CXP pulse generator allows address modification to execute programmed jumps. Figure 5 gives a schematic representation of the interconnections between the most important components.
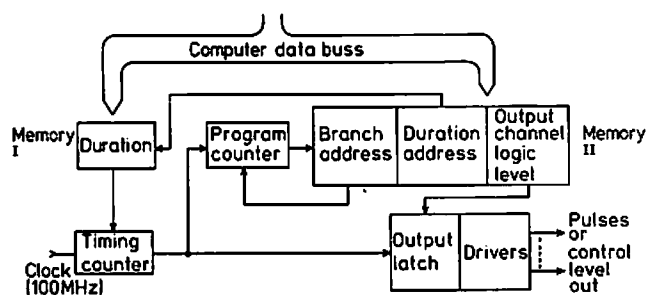

Figure 5 Advanced software controlled pulse programmer.

There are other software controlled pulse generators which should be mentioned. Lapray *et al* (1976) store only timing data in a memory, a hard wired program logic selects the needed values to produce a pulse sequence. In contrast to this Toms (1974) stores only level and address jump information in a shift register memory that circulates constantly and establishes in this way the time intervals. Caron and Herzog (1978) report on a programmable timer which works in a similar way to the TS mentioned before but also allows sub-burst generation by looping. Another interesting feature is a circuitry inserted to provide the possibility for synchronisation with several external events.

Finally one may ask: how is the memory loaded? This can be done in several ways. With most devices it is possible to do this via front panel switches. Also card or paper tape readers may be interfaced. The most flexible configuration is obtained when interfacing a micro- or minicomputer. This allows not only easy loading of the memory, but also a very efficient utilisation of the so-called dynamic updating feature, which permits the changing of information in the memory |while the pulse program is being executed. In this way very powerful and easy to handle pulse sequence generation facilities can be obtained. Pure software pulse generators and hardware supported software pulse generators will be treated in the next chapters.

3.2.3 Transmitter In the early 1960s it was found that instabilities, in particular during multiple pulse sequences consisting of many pulses with a relative phase difference, as e.g. CPGM sequences, could be overcome by synchronisation of pulse programmer cycle and transmitter RF. This means that all RF pulses, including repeated sequences, which come from the same gate automatically start at the same point on the RF wave form. Thus Holz (1966) used the same quartz controlled master oscillator both as clock for his digital pulse programmer as well as RF source. This principle was then used in the commercial Bruker B-KR 300s spectrometer series. Today even the variable frequency spectrometer with a

synthesiser as RF source are completely controlled (including computer cycle) by one quartz oscillator and thus synchronised. The main advantages of this 'coherent spectrometer operation', which were discussed by Mehring and Waugh (1972), are phase stability and stability of the effective RF pulse length. As pointed out by Karlicek and Lowe (1978) fully coherent operation requires the fulfilment of some relations between operation frequency, repetition rate of the sequence and pulse distance.

In order to be able to produce RF pulses of different phase, the CW carrier from the RF source is normally divided into four branches since sophisticated pulsed spectrometers should be able to deliver RF pulses with 0°, 90°, 180° and 270° phase difference. In the beginning of pulsed NMR the phase differences were obtained by commercially available variable delay lines or coaxial cables of different lengths. These phase shifters are unsuitable for variable frequency operation and not very precise. Ellett *et al* (1971) used air dielectric coaxial line stretchers for fine phase trimming for a fixed frequency spectrometer. The automatic generation of the four phase differences in variable frequency instruments is described by Ellett *et al* (1971) and by Karlicek and Lowe (1978), who used commercially available 'power splitters' whose outputs are phase shifted relative to one another. The complete network consists of a 90° hybrid junction and two 180° hybrids as shown in figure 6. For the final precise phase setting Ellett *et al* (1971) added voltage controlled varactor phase trimmers. Varactor phase shifters could be successfully used in the commercial Bruker SXP and CXP spectrometers to achieve the total phase differences.
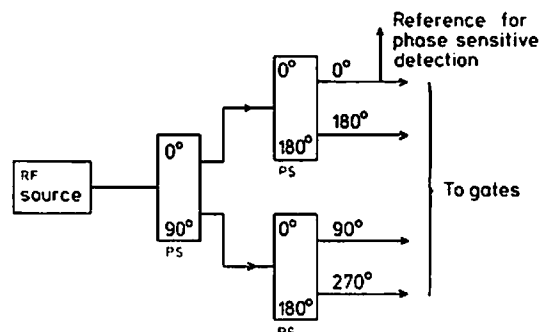

Figure 6 Four-phase generation in pulsed NMR spectrometers from a common RF source. (PS = power splitter, 0°, 90°, 180°, 270° are the phase differences.)

After phase shifting the different CW carriers are then gated by four broadband double balanced mixers, which today are used as gates in most pulsed spectrometers. The RF pulses generated in this way are thereafter separated in time and may then be given via a combiner to a common driver stage and power amplifier where up to some kW RMS of pulse power are produced.

Frequency variability is of great importance for many experiments e.g. frequency dependent relaxations studies, multinuclear research or NMR in ferromagnetic materials. Therefore many frequency variable systems have been described, for example, by Ellett *et al* (1971) (20–250 MHz), Narath and Barham (1974) (2–200 MHz), Khoi and Veillet (1974) (170–1700 MHz) and recently by Karlicek and Lowe (1978) (5–90 MHz). The commercial spectrometers Bruker CXP cover the frequency range 4–125, 188–200 and 282–300 MHz. For double resonance cross relaxation experiments

Ackerman *et al* (1975) developed a device for rapid changes in transmitter frequency without loss of phase coherence using digital synthesis technique.

A high on/off ratio characterises a good transmitter for pulsed NMR. An interesting solution of this problem has been described by Radeka *et al* (1970). They built a digital RF generator, where the frequency of interest is obtained by mixing two higher frequencies, thus in the off intervals no signal of the NMR frequency is present in the entire generator system. Since the output frequency is derived digitally, they are able to introduce a 90° RF phase shift digitally, which is an elegant alternative. Another important point of the transmitter is its ringdown time, which should be as small as possible, since the kV pulse is immediately followed by a μV NMR signal to be detected. Transmitter ringdown increases the deadtime of the receiver system and thus prevents signal observation during this time. Therefore a number of switched damping circuits have been proposed in the literature, which automatically switch the Q of the transmitter coil in the probe to lower values after the pulse. Clark (1964), Spokas (1965), Samuelson and Ailion (1970) and Kisman and Armstrong (1974) applied diodes where the impedance is varied by controlling the bias current, whereas Conradi (1977) used a field effect transistor. But it should be mentioned here that in general the danger exists that spurious signals may be introduced by those switched probe dampers.

3.2.4 *Signal detection* Minimising of the recovery time following the overload by the RF pulse is an old problem in pulsed NMR, which is particularly important for solid state investigations. Therefore, besides the probe damping, automatic receivers blocking schemes have also been developed, for example by Lowe and Tarr (1968), Grannell *et al* (1973) and Hoult and Richards (1976). The latter authors treated the problem of receiver protection at frequencies above 100 MHz and used PIN diodes as switching elements in a circuit which gives good isolation of the transmitter from the receiver. For example, the blocking gate used by Karlicek and Lowe (1978) shortened the recovering time to $\sim$0·5 μs at 60 MHz.

In connection with FT NMR the use of quadrature detection, that is, simultaneous detection of NMR absorption and dispersion signals by two perfect orthogonal phase sensitive detectors, has great advantages (see Stejskal and Schaefer 1974a, b). Both channels must, however, have identical amplitude and exact 90° phase difference. Therefore it is important to have automatic correction of errors which are present in practice and which produce reflected lines in the transformed spectrum. There are two ways to overcome this problem. A number of authors as e.g. Jeener and Segebarth (1975) and Parks and Johannesen (1976) used software correction of the stored signals prior to Fourier transformation. The necessary information about the degree of misalignment may be derived from a single symmetric NMR absorption line or from noise correlation measurements in the two channels (without signal!). The second way, often used, has been described by Stejskal and Schaefer (1974a, b). As suggested by R E Richards (see also Hoult and Richards 1975) the reflections can be removed by RF phase shifting together with appropriate data routing. Stejskal and Schaefer (1974a, b) applying a two-pulse cycle with 90° phase shifted pulses demonstrated the cancellation of quadrature errors.

3.2.5 *Data acquisition* Digital data acquisition is a general task in laboratory automation. In connection with pulsed NMR, problems concerning the choice of appropriate sampling rates or the required resolution of analogue-to-digital conversion devices are treated in several monographs, e.g. Farrar

and Becker (1971) or Cooper (1976). A wide-spread method is the use of time averagers. These are hard-wired special purpose minicomputers available in various commercial designs which include an ADC, an arithmetic unit to add successive signals for signal-to-noise ratio improvement, a memory to store these signals in a digital form and output possibilities (display, plotter connections, data channels to paper tape punch or to other computers). An inexpensive signal averager designed for pulsed NMR using an analogue memory has been described by Larsen and Windsor (1975). Holz and Thiel (1980) built the same instrument but added a digital memory enabling the digital display of the integral or amplitude of the NMR signal. Another device, which is useful when very fast signals have to be digitised, and which is specially appropriate in connection with the use of a minicomputer, is a so-called 'transient recorder'. A large number of commercially available instruments cover a broad spectrum of resolution, speed and memory capabilities. Conversion rates of up to 500 MHz (with 6 bit resolution) are realised. Recently a list of commercially available models appeared in the Journal *Markt und Technik* (1979).

These transient recorders do not have the possibility of signal accumulation. Usually they store the fast 'transient' signal in a shift register, from where it can be read out during the delay time between successive pulses by using a slower minicomputer to accumulate the signals. Such a simple and quite inexpensive system is described by Merrick *et al* (1974). It may now be possible to use such transient recorders in connection with 'personal computers' to get an even less expensive system, good enough for a large number of applications. A low cost enhancement of the effective sampling rate of a commercial transient recorder, by interleaving successive records in the memory of a small computer, has been developed by Landers *et al* (1978).

Venhuizen and Sawatzky (1976, 1978) discovered two different ways of using 'time base expansion' and normal multichannel analysers in connection with very fast transient signals. In their first paper the photoconductive coating of the vidicon tube inside a TV camera directed towards an oscilloscope tube is used as buffer memory to translate the fast information into a much slower video signal. In their second paper the analogue memory into which the fast signal is read consists of a series of capacitors, from which the signal can be read out later at a slower rate, a principle similar to that of Larsen and Windsor (1975).

In classical pulse NMR experiments storage oscilloscopes are often used to measure the signal amplitude. Naturally the accuracy of those measurements is limited. The above mentioned units provide a higher accuracy but are often expensive. A simple inexpensive integrating digital unit which consists of gated integrator, timing circuit and ADC, designed for pulsed NMR has been described by Sandhu (1974) and such a device may represent a reasonable compromise for most pulsed NMR experiments.

3.2.6 *Temperature control* It is surprising that in the highly sophisticated NMR instrumentation, the weakest point of the entire system is often the sample temperature control system. In most cases, even in commercial systems, the desired temperature is obtained by a stream of preheated or precooled gas, and the temperature is measured using a thermocouple near the sample. This technique often gives rise to errors caused by temperature gradients e.g. over the sample volume which produce differences in sample and thermocouple temperature. Kollie *et al* (1977) also pointed out that with Chromel–Alumel thermocouples, due to the Ettinghausen–Nernst effect in the magnetic field, additional errors may be

caused. More precise temperature control systems in pulsed NMR use liquids as thermostatic baths (see e.g. Harris *et al* (1978)) or as a thermostat medium for the complete probehead or parts of the probehead (see e.g. Norris and Strange (1969)). A high temperature furnace (to 1300 K) has been described by Gordon *et al* (1978).

Automated temperature dependent measurements may be performed if the computer of the NMR system can control the setting of the variable temperature unit. After the desired number of measurements at constant temperature the computer then switches to the next programmed temperature. Such automated measurements have been performed by Geiger and Hertz (1976) and are today also possible with the commercial Bruker CXP instrument. Level control and automated refilling of liquid nitrogen in Dewar vessels which are used for low temperature measurements, as for example described by West (1974), should also be mentioned here as a possibility of automation in temperature control systems.

4 System automation

4.1 Interfacing and instrument control

For a few years sophisticated computerised pulsed NMR spectrometers have been readily available, but there also exist a large number of old, simple and relatively inexpensive systems (commercial as well as home built) which suffer from a lack of digitisation and a dependence on manual operation. Interfacing these instruments to computers can greatly enhance their performance. As mentioned in the introduction, the main task of such automated systems is to generate pulse sequences, to control adjustment of parameters, to collect data and to perform the necessary calculations.

Several publications describe computerised pulsed NMR systems, the extent of automation varying strongly. Figure 7 shows as an example the block diagram of a system described
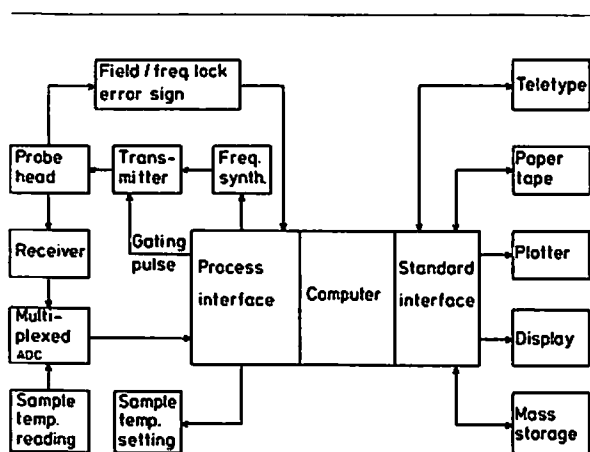

Figure 7 Block diagram of a computerised pulsed NMR system.

later. In the simplest versions the computer is used only for the final data storage and processing. The system of Gerig *et al* (1973) is an example: the pulse sequence is generated by the spectrometer, as is also the triggering of the time averager and computer. To get synchronous operation, the number of pulse sequence repetitions must be set independently in the computer and in the spectrometer. After accumulation the signals are integrated between preselected limits, normalised and then the collected data are used to evaluate the relaxation time by a least square fit. Finally the experimental and fitted data are compared visually by using the display features of the

time averager. A similar system is described by Giezendanner *et al* (1975).

Rhodes *et al* (1973) eliminated the time averager. They describe a computer interface, which includes an ADC. The computer starts the pulse programmer of the spectrometer which in return delivers a suitably timed trigger impulse. This one starts a computer routine which operates the ADC under software control: the ADC is initialised, then the computer waits until conversion is terminated. After that the obtained value is read, added and stored in the computer memory. By this procedure the signal is traced out point by point. Finally the computer displays the digitised and accumulated results on an oscilloscope via a digital-to-analogue converter.

For many applications, this software controlled A/D conversion is not fast enough. Križan (1975) describes a microcomputer interface which performs the timing of the NMR signal sampling, the analogue-to-digital conversion and the intermediate storing of the signal. In this way a sampling rate of 100 kHz was achieved. The transfer of the stored data into the microcomputer for further processing can then be done at a slower rate during the waiting period between two successive pulse sequences. (One should mention here that in recent systems fast analogue-to-digital conversion and transfer of data to the minicomputer memory is performed under the hardware control of a direct memory access data channel (DMA).) Another feature of this interface is the incorporation of an up/down counter to measure the time between 90° and 180° pulses (produced independently by the spectrometers PP) and to delay ADC start until appearance of the spin echo.

In the systems described up to here, the generation of pulse sequences is only triggered by the computer. Next we will discuss systems where the pulse sequence is influenced or totally produced by the computer. Wright and Rogers (1973) and Huang and Rogers (1977) use a pure software pulse generator. That means that the basis of the timing clock is the definite execution time of the software instructions in the program and that the time intervals are produced by software counters. In this way time intervals greater than 1 ms have an error of less than 0·1 %, the shortest possible time interval being 26 μs. Via I/O instructions pulses are produced to trigger monostable multivibrators. The length of each monostable pulse is varied manually to form 90°, 180° or magnetic field gradient pulses. Also a phase shifter is triggered in the same way.

While in normal time averaging procedure identical pulse sequences are repeated N times, Huang and Rogers (1977) vary the pulse sequences successively until the total measuring range is scanned, then this is repeated N times, adding corresponding signals. By this method drift effects (e.g. field drifts) are reduced. Huang and Rogers also describe the application of hybrid relaxation time measurements: Special pulse sequences allow the measurement of both T_1 and T_2 in a single scan which is interesting when measuring long relaxation times, although the accuracy is not very high.

A software pulse generator is also used in the system described by Geiger (1973) and Hermann (1974). Figure 7 gives a schematic survey of the total arrangement. The time base to produce proper intervals between gating pulses is given by hardware interrupts of the programmable computer clock rather than by the execution time of software instructions. Pulse width is controlled directly through the computer by using a digital counter with multiplexed output. Another interesting feature is the field/frequency lock mentioned in §3.2.1. An extended version of the system is described in the next section.

As mentioned before, in the field of pulse sequence genera-

tion the most promising line of development is the use of hardware pulse generators, operating under software control. The pulse programmers of Ellett *et al* (1971) and of the Bruker CXP series described in §3.2.2 are both part of a computer controlled system, one of the main functions of the computer being the servicing of the pulse programmer.

A convenient and inexpensive version of this conception is the use of a microprocessor to control the time interval settings in a commercial multipulse generator via latched BCD-lines (Ader *et al* 1978). Here, the data acquisition module as well as the programmable clock are supervised by the microprocessor. Only one data point per NMR signal is sampled, accumulated and stored in a random access memory (RAM). Subsequently data may be transferred to a remote computer over telephone lines.

Cantor and Jonas (1976, 1977) developed a system which is not only able to execute the usual functions like pulse sequence generation, data collection, data evaluation, but which also offers the possibility of optimising experimental parameters. This is, for example, necessary when performing series of measurements over wide ranges of pressure and temperature. In this case marked changes of electrical parameters in the NMR sample probe demand frequent reoptimisation of pulse lengths and phases. To do this requires the use of a software controlled pulse generator including pulse length variation. Cantor and Jonas use four independent cascaded digital timers in A-t_1-B-t_2 sequence (A, B, pulses; t_1, t_2, delay times), driven by a 10 MHz clock with gated divider circuits. A trigger control logic may disable either of the pulses and retrigger the sequence at any point. Thus complex pulse sequences may be generated. Phase control is achieved by two latched digital-to-analogue converters which control a pair of voltage-variable phase shifters.

The test function for optimisation is the integral over some part of the FID. A one-dimensional sequential search algorithm (King and Deming 1974) finds the optimum parameter setting within 8 to 12 steps. The reproducibility is within $\pm 0.2 \mu s$ for the pulse length and $\pm 2°$ for the phase. Thus the precision of the system is increased in comparison with manual operation. Replication of T_1 values lies between 1 and 4%, diffusion coefficients have an accuracy of 5% and a reproducibility of 1 to 4%. The magnetic field gradient calibration procedure, which is important for diffusion coefficient measurements, was also performed under computer control.

4.2 *Computational procedures*

With a computer interfaced to an NMR experiment mainly for control purposes as described before, the additionally gained computational possibilities may also be used for data evaluation. Two particular goals were envisaged: (i) increasing precision of relaxation times obtained from 'ordinary' pulse sequence experiments, (ii) using new time-saving pulse methods, which require more complicated calculations to derive the desired relaxation data. As examples some recent papers will be discussed. References to earlier papers will be found in Leipert and Marquardt (1976) and Hanssum *et al* (1978).

The first problem reduces in many cases to the question, how to analyse mathematically a noisy exponential with an arbitrary baseline. Several papers stress the superiority of iterative exponential fitting compared to linear regression analysis of semilogarithmic data (Leipert and Marquardt 1976, Gerhards and Dietrich 1976, Sass and Ziessow 1977). Strehlow (1978) describes a comparatively simple technique for the evaluation of parameters, when a superposition of more than one exponential is present. A list of references concerning different methods is also given in this paper.

Digital filtering is another category of data processing. Smith and Cohn-Sfetcu (1975) examine problems associated with its use and discuss a method, which is particularly interesting for FID filtering: signals which start discontinuously but decay slowly to zero are distorted only minimally when 'reverse time filter' is applied. On the other hand Matson (1977) investigated the optimum procedure, when integrating over portions of the FID, for signal-to-noise ratio improvement. Another field of data manipulation to increase precision of measurement is the correction of phase errors when using quadrature detection as described in §3.2.4.

Many authors have developed time-saving methods at the experimental and computational levels. A useful reference list for the different methods is given by Hanssum *et al* (1978). These authors describe a least square procedure to fit fast inversion-recovery sequence data. A similar procedure is given by Brunetti (1977). Edzes (1975) concentrated on single scan determination of spin–lattice relaxation rates.

5 Automation of a pulsed NMR laboratory

Many laboratories are equipped with more than one pulsed NMR spectrometer, one reason being the fact that previously only fixed frequency spectrometers were built. When several spectrometers have to be computerised simultaneously there arises the question of optimal strategy. This is a general question in laboratory automation and was treated earlier in a review article of this journal (Millett 1976). Three basic principles may be distinguished. In the most simple case each instrument is controlled by its own ('dedicated') minicomputer. This was described in the previous section. In the opposite extreme a single computer is shared among several users. A third possibility is the interconnection of several processors ('distributed system') so that different tasks like real-time data acquisition and data handling may be treated by separate processors.

The reason for constructing a time-shared system is clear: depending on the relaxation time of the sample to be measured and the pulse sequence used, the computer spends most of its time waiting and doing nothing. That means that, from the standpoint of time demand, most minicomputers should be able to service several spectrometers synchronously, or, to be more specific, service one spectrometer during the waiting period of the others. It is clear that timing conflicts will occur and that their solution will diminish the availability of the computer for the individual spectrometer compared to a dedicated computer. This disadvantage is avoided in a multiprocessor system. Relatively sparingly equipped mini- or microprocessors are allocated to each spectrometer for real-time control and data acquisition. They are connected to a central computer which is equipped comfortably for data handling (I/O, display, plotting facilities, mass storage). This distributed system is preferable to the shared system, even for economic reasons, because computer hardware prices have reduced drastically during recent years. Moreover, a shared system demands a specially tailored real-time operating system, whereas the central computer of the distributed system can use a standard operating system. Both shared and distributed systems are less expensive than an assembly of dedicated computers, where each one needs sufficient peripheral equipment. Bearing this in mind it is astonishing that, to our knowledge, until very recently (Wright 1979), practically no publications on NMR laboratory automation can be found. Thus a short description of the system developed in our laboratory will be given (unpublished DFG report, catalogued in *Deutsche Forschungsber* 3 (1974), AC 1601 and AC 1100).

The starting point was the dedicated system of Geiger (1973) and Hermann (1974), mentioned in the previous

section. To service three different NMR spectrometers simultaneously, each of three experimenting places was equipped with a dialogue teletype, sensor switches to influence the course of the program, pulse outputs to control the instruments, digital-to-analogue converter outputs for display purposes and ADC connections to input the analogue signals to be measured. The ADC input responsible for the gating pulse counter and output is directed to the desired experiment by multiplexers, whereas the other equipment of the computer is present in parallel in sufficient quantity. To eliminate ground loops the pulse, digital-to-analogue and analogue-to-digital lines were connected to the computer via optical coupling devices. This is easily achieved in pulse lines. To get the necessary linearity of these circuit for the analogue signals a pair of matched optocouplers had to be used in a negative feedback configuration. The computer software is divided into two sections: a real-time executive part (RTE) and a dialogue and control program (DCP). The interconnection between both parts is established by lists and flags (this program organisation is indicated in figure 8). DCP is written to be used re-entrantly
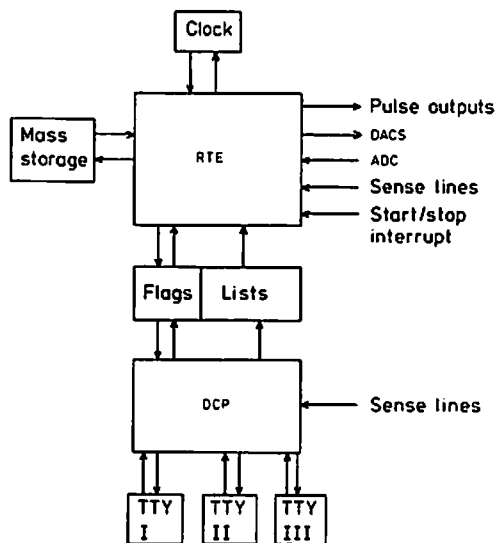

Figure 8 Program organisation for a multi-spectrometer system.

in a multi-tasking way, so that for each spectrometer the DCP is executed on a different interrupt level (according to the attached dialogue teletype), using separate registers and memory areas. The communication with all interface units which have to be shared by the three spectrometers or whose utilisation is critical in time is achieved by RTE. The most important unit is the computer clock. This may be programmed to give a level restart after a preselected time which may vary between 1 μs and 327 s (in steps of 1 μs to 10 ms). In this way pulse separations are produced with an accuracy of 1 μs. RTE is executed on high priority levels compared to DCP. According to the pulse experiment required, the DCP generates a control string which will be executed by RTE after a specified waiting period. The control strings are composed of several 'pulse tables', each containing the following seven parameters: (i) pulse channel; (ii) pulse length; (iii) ADC start delay time; (iv) ADC channel; (v) number of data points to be used successively; (vi) memory address for data string; (vii) delay time before next pulse.

This string is interpreted by RTE as follows: after a demanded waiting period (recovery time which may eventually be

extended by RTE to avoid overlapping of crucial time periods) RTE transmits a gating pulse of specified length via the pulse channel indicated in the list. When the ADC start delay is over, a series of data points is read into the given memory region (via direct memory access) with a rate of 100 kHz. If the pulse delay time is set zero, the end of the control string is indicated, if not the next pulse table is executed at the end of the desired pulse delay. New pulse sequences can easily be introduced by modifying the construction of the control strings. The complicated and time-crucial RTE may be left unchanged.

Control strings may be executed in two different modes of DCP. In the so-called adjust mode these strings are repeated continuously (observing the preselected waiting periods). Simultaneously, in a real-time multiprogramming manner all parameters may be altered by simple teletype instructions. It is the purpose of this mode to find optimum parameter settings by observing the analogue as well as the digitised and accumulated signals on an oscilloscope. Having determined these parameters DCP may be switched to the measuring mode. Now the computer executes independently a measurement, automatically varying pulse spacings and performing the required signal accumulations. The results are stored for subsequent processing. The application of two pulses as well as saturation recovery sequences have been implemented, also the control of a pulsed field gradient apparatus for diffusion coefficient measurements (Kuss 1975).

The system of Wright (1979) may be considered as a simple version of a 'distributed' system. Each spectrometer is equipped with a programmable pulse generator ('timing computer') similar to that described by Toms (1974). A central minicomputer programs and controls these satellite controllers. They do not contain digitiser and memory, but have to share the data acquisition channel of the minicomputer. For this reason the central computer monitors alert lines by which the satellites demand servicing. Data may be missed when more than one spectrometer is in operation because the computer is busy at the wrong time (this increases the total operation time), but the correct timing for a given pulse sequence is always maintained by the dedicated timers. The author investigated carefully the performance of the time sharing system. He showed that this simple arrangement is nearly as efficient in many cases as a dedicated minicomputer for each spectrometer.

6 Pulsed NMR spectrometers in industrial processing

The utility of NMR as a routine method in industrial process and quality control had been recognised very early. Meanwhile a great number of publications appeared in which, in particular, the applications in food science were described and recently this field has been reviewed by Weisser (1977). The first instruments used for this purpose were simple wide line apparatus. However, as van Putte and van den Enden (1973), for example, pointed out, the wide line technique has some distinct disadvantages, which can be overcome by pulsed NMR. Therefore in the 1970s simple commercial pulsed NMR systems found entrance into the research laboratories and production control of the food industry. In particular, instruments were developed for quick and automatic determination of the solid fat content in fats as an alternative to the slow dilatometer technique. The method is based on the fact that the FID from protons in the solid state decays much faster than the FID from protons in the liquid oil. Therefore, directly after the 90° pulse both solid and liquid contribute to the signal, whereas about 100 μs later only the liquid signal is still present. Van Putte and van den Enden (1973 and 1974) used a Bruker B-PA16 instrument and determined, with two Boxcar integrators, the signal amplitude 14 μs and 70 μs after the

90° pulse. After appropriate signal processing the solid fat percentage was displayed on a digital voltmeter and printed out. Meanwhile a new commercial instrument (Bruker minispec p 20) is obtainable, an almost completely automated small pulse spectrometer with permanent magnet, digital readout and printer, which is able to perform the above described tasks. It is a microprocessor controlled instrument with more flexible pulse programming. The data evaluation is also performed under microprocessor control. The instrument may be equipped with an automatic sample transfer device, which allows the automatic measurement of 96 samples. The samples are located on a digitally controlled turn-plate from which the sample falls into the probe head. After measurement the sample falls into a container below the probe head and the next sample can be measured. Madison and Hill (1978) described the automatic solid fat content determination with a Model SFC-900 of Praxis Corp., a pulsed NMR system with special emphasis on sample tempering and temperature dependent measurements. This instrument is equipped with six 10 mm sample locations with different temperature for both sample conditioning and measurement.

Taking into account the rapid development of the microprocessor technology and having in mind the great number of further possible applications of pulsed NMR as for example flow and diffusion measurements or tomographic NMR (see the review of Singer (1978)), it is easy to predict that in future an increasing number of automated pulsed NMR systems, tailored for special tasks, will be installed for industrial applications.

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