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Techniques involved in the study of Different Nuclei by high Resolution Nuclear Magnetic Resonance

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1. INTRODUCTION.

The application of nuclear magnetic resonance to the solution of chemical problems is increasing rapidly and is being extended to a wide variety of compounds. The majority of work published has been on hydrogen and by comparison very little on any of the hundred or so other nuclei which are capable of the nuclear magnetic resonance phenomenon. Perhaps one reason for this is that present instruments are not too well suited for the study of different nuclei, the change from one to another being either difficult or expensive.

In the first part of the paper some of the familiar features which distinguish the nuclear magnetic resonance spectra of the different nuclei are surveyed and their influence on the design of a comprehensive spectrometer considered. In the second part, a brief account of our approach to the problem is given with illustrations of some of the techniques used.

2. CONSIDERATION OF THE FACTORS INVOLVED.

It is well known that hydrogen is characterised by very small natural line widths and that the highest resolution is required in order to observe the small chemical shifts, sometimes less than 0.1 p.p.m. and seldom more than 10 p.p.m., and the correspondingly small spin-spin coupling constants, sometimes less than 0.01 p.p.m. Although hydrogen has one of the strongest resonances, many of its compounds, and often those of most interest, have high molecular weights so that high sensitivity is also important in order to observe individual protons or groups. Thus for the optimum study of hydrogen spectra it is not only necessary to have high resolution but also desirable to have this high resolution available at high magnetic fields, for two reasons: firstly, the intensity of the resonance increases

and, secondly, the ratio between the chemical shifts and spin-spin coupling constants increases with field.

Fluorine, like hydrogen, exhibits narrow lines and strong signals, although its chemical shifts are much larger, in some cases approaching 700 p.p.m. These shifts are accompanied by large spin-spin coupling constants, but often they extend to nuclei three or four bonds removed, giving rise to complicated and closely spaced fine structure. Thus, to obtain the maximum information from a fluorine spectrum, the highest resolution is frequently required. Also the presence of fluorine in large molecules and the sub-division of individual lines into complex multiplets makes it desirable, for reasons of sensitivity, to operate at high fields.

Hydrogen and fluorine resonances occur at similar fields but in order to cover as large a range of nuclei as possible and to operate at the optimum magnetic fields it is essential to have available a number of different frequencies. It is important to take this into account at an early stage in the design of the r.f. circuitry.

By comparison with hydrogen and fluorine, other nuclei have inherently low signal strengths. This is particularly serious if the isotopes capable of nuclear magnetic resonance have low natural abundances, for example O^{17} and C^{13} , or if the line is broadened due to the presence of a nuclear quadrupole moment. Here again, high fields are desirable on the grounds of sensitivity. However, most of these nuclei have broader lines and the demand on resolution is not so exacting as with hydrogen and fluorine so that larger samples can be used without the homogeneity of the field over the sample volume exceeding the natural line width. The probe, therefore, should be designed to accommodate readily large as well as small sample tubes. In addition, field or frequency modulation at low frequencies can often be used with a lock-in detector and filtering to increase the signal to noise ratio by drastically reducing the receiver bandwidth. These features are essential if a wide range of nuclei is to be studied.

With nuclei other than hydrogen the chemical shifts are large and thus large sweeps must be provided; for example, shifts of up to 1.5% have been reported for cobalt and in extreme cases shifts of up to 15% for lead.

There are certain cases, with all nuclei, when it is an advantage to examine compounds at temperatures other than room temperature. For instance, by raising the temperature, a low melting point solid can be liquefied and, therefore, examined by high resolution, the viscosity of a

liquid can be reduced in order to show fine structure or the concentration of a solute can be increased to improve sensitivity. Also, by varying the temperature, certain specialized topics such as hindered rotation and tautomerism can be studied. It is therefore important to bear this in mind when the design of the probe is under consideration.

This brief discussion has shown that several techniques must be provided if a nuclear magnetic resonance spectrometer is to be used for the study of different nuclei. The most important requirements which have emerged are those of high magnetic fields, high resolution, a probe design capable of being easily adapted to different frequencies, different sizes of sample tube and temperature variation, and r.f. circuitry which provides an easily interchangeable series of radio-frequencies and detection systems.

3. DESCRIPTION OF THE TECHNIQUES USED.

3.1. *General.*

The emphasis of this work has been to integrate the different techniques required in high resolution spectroscopy into a single instrument. The techniques are not new in principle but the combination produced represents a new approach to the problem of studying difference nuclei. The techniques have been developed on a prototype version of the A.E.I. R.S.2. nuclear magnetic resonance spectrometer. This is based on the use of a bridge and single coil system and employs a high field, high stability electromagnet, which for standard use is equipped with 11" diameter pole shoes tapering to 9" and a gap of 1½". It provides a continuously variable field from 1,000 to 18,000 gauss.

3.2. *Stability and Homogeneity of Magnetic Field.*

To satisfy the exacting requirements of hydrogen, a resolution of 1 part in 10^8 is necessary at high fields. One of the greatest difficulties is to provide sufficient stability and homogeneity of magnetic field over the sample volume at values of the order of 14,000 gauss. Current stabilization in excess of 1 part in 10^6 is difficult and because, in any case, variations in the local magnetic fields in the neighbourhood of the magnet cannot be compensated in this way, additional short term stabilization has been provided for by an electronic flux stabilizer. Two pairs of coils are located close to the magnet gap; small changes in the flux through the first pair induce small e.m.f.'s which are amplified and fed, after phase adjustment,

to the second pair. The method is similar in principle to that described by Primas and Gunthard (1957) and provides sufficient stability to obtain the required resolution of 1 part in 10^8 . Unfortunately the induced voltages are proportional to the rate of change of the flux, so that variations of 1 part in 10^9 over a minute or 1 part in 10^8 over several minutes cannot be distinguished from the inherent thermal noise of the pick-up coils and detecting system. There appear to be two main causes of long term variations, namely, minute variations in the dimensions of the magnet yoke with temperature and variations in the BH product of the iron with time, especially in the vicinity of the gap. It has been found that the latter effect is more pronounced immediately after a large field change, but by working at high fields this can be reduced. To reduce the effects of variation in yoke dimensions all the exposed portions of the magnet have been thermally insulated with a heavy lagging of polystyrene foam, enclosed in a fibre glass cover, and the main current coils completely insulated from the magnet limbs by a water jacket and air gap.

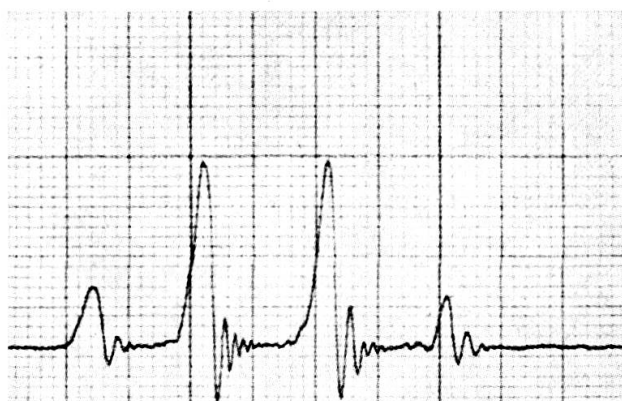
A number of the standard high resolution techniques have been employed to obtain the required homogeneity. These include the use of optically polished pole shoes which are accurately aligned during assembly, and a spinning 4.5 mm o.d. sample tube. However, at high fields, even with a relatively high ratio of pole diameter to gap width, the increased flux densities at the edge of the pole shoes can give rise to a quadratic field distribution at the centre. Also small temperature gradients across the magnet yoke can produce a non-linear field distribution by introducing a slight non-parallelism of the pole shoes. It has been found possible to correct for both these effects with current shims mounted on the probe. The design of the current shims is somewhat similar in principle to that described by Golay (1958).

3.3. *Resolution at Different Magnetic Fields.*

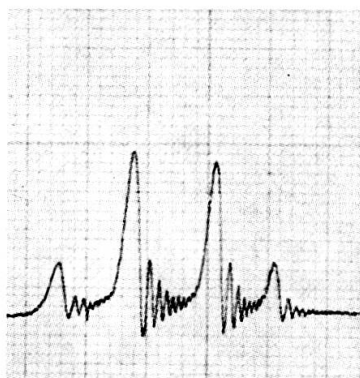
At fields above 13,000 gauss it has been found that « cycling » of the magnet has little effect on the field distribution. This is probably due to the reduction in the area of the hysteresis loops at high fields. At fields below this, « cycling » has again been found unnecessary as the current shims are simpler to operate and equally effective.

At 14,092 gauss (H^1 at 60 Mc/s) the resolution obtained has been consistently 1 in 10^8 . Figure 1a shows a trace of the —CHO quartet of a sample of vacuum distilled acetaldehyde in a 4.5 mm o.d. spinning tube

(the coupling constant for these peaks is 2.85 c/s.). A spectrum of a similar sample in a larger volume and at a lower field is shown in figure 1 *b*; it is a recording of the quartet of acetaldehyde in a 9 mm o.d. spinning sample tube at a field of 9,395 gauss (H^1 at 40 Mc/s).



a) 4.5 mm o. d. Spinning Sample (60 mc/s)



b) 9.0 mm o. d. Spinning Sample (40 mc/s)

Fig. 1.

The CHO quartet of acetaldehyde at different frequencies.

Figure 2 shows a spectrum of 1:1:2-trifluoro 1-bromo 2-chloroethane taken in a 4.5 mm o.d. spinning tube at 14,979 gauss (F^{19} at 60 Mc/s) where the line width is slightly in excess of 1 part in 10^8 . This compound illustrates the relatively large shifts compared with hydrogen, the multiple splitting and the presence of small peak separations. An extensive study of the hydrogen and fluorine spectra of this compound has been made by Lee and Sutcliffe (1958).

3.4. *Probe Design.*

The idea underlying the development of the probe was to produce a universal system that could be used at different frequencies with different sample tubes and for variable temperature studies. The design finally evolved consists of a major assembly, which remains unchanged in all

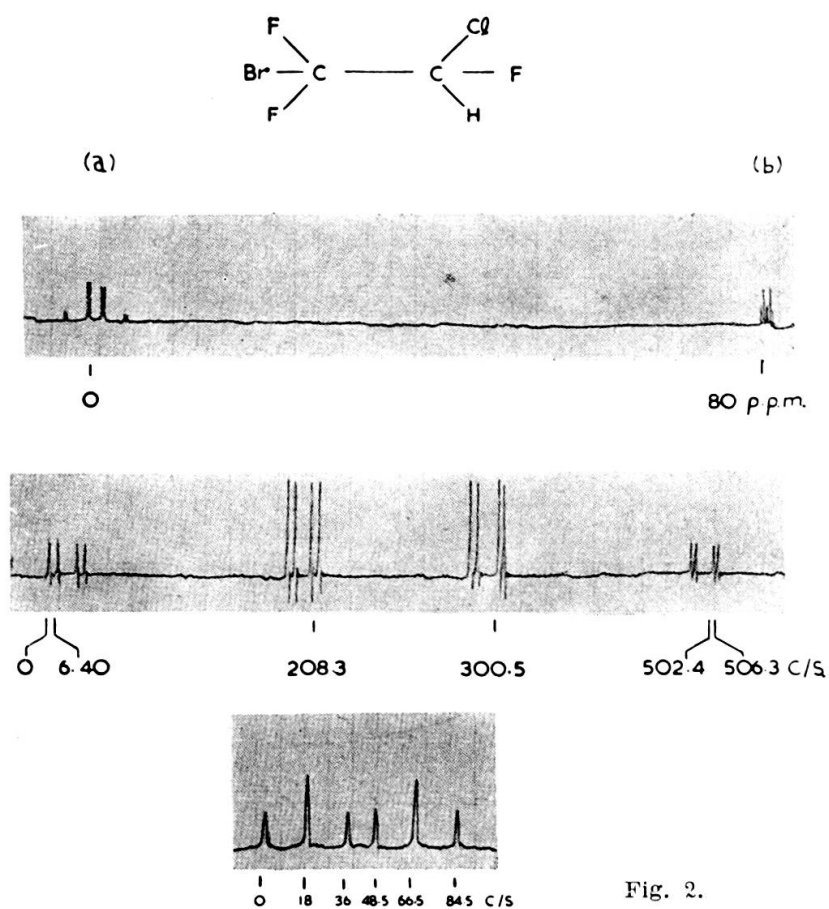


Fig. 2.

Fluorine resonance spectra of 1:1:2-trifluoro 1-bromo 2-chloroethane at 60 Mc/s, (a) CF_2Br group and (b) CFCIH group.

applications and into which the appropriate sample coil insert and pre-amplifier «box» are placed. The latter contains the bridge and pre-amplifier which is fitted, like the sample coil insert, with a plug-in connection for easy replacement by a different frequency unit. In this way it has been found possible to accommodate in a single design the following:—

- (i) a 4.5 mm o.d. spinning sample tube;
 - (ii) a 9.0 mm o.d. spinning sample tube;
 - (iii) a 15.0 mm o.d. non-spinning sample tube
- and (iv) a variable temperature insert which takes a 4.5 mm spinning sample tube.

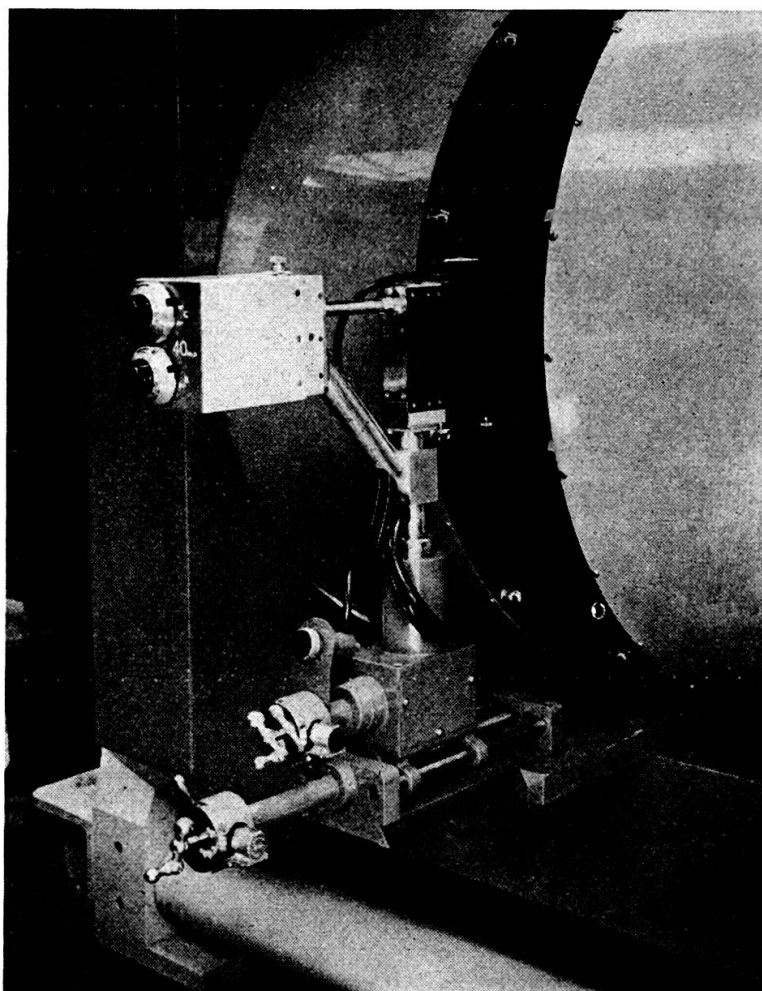


Fig. 3.

The probe and moving mechanism of the R.S.2 withdrawn from the magnet gap.

A photograph of the probe and moving mechanism withdrawn from the magnet gap is reproduced in figure 3 and a photograph of four inserts and two pre-amplifier boxes is reproduced in figure 4.

The probe assembly also accommodates the current shims and two pairs of coils, which approximate to a Helmholtz configuration. One of

these coils is fed from a saw-tooth generator and provides a repetitive sweep, the other is fed from a low frequency oscillator for side-band calibration, or use with the «lock-in-detector». There are two principal reasons for mounting the current shims on the probe block rather than on the magnet: (i) with the type used, the best results are obtained if

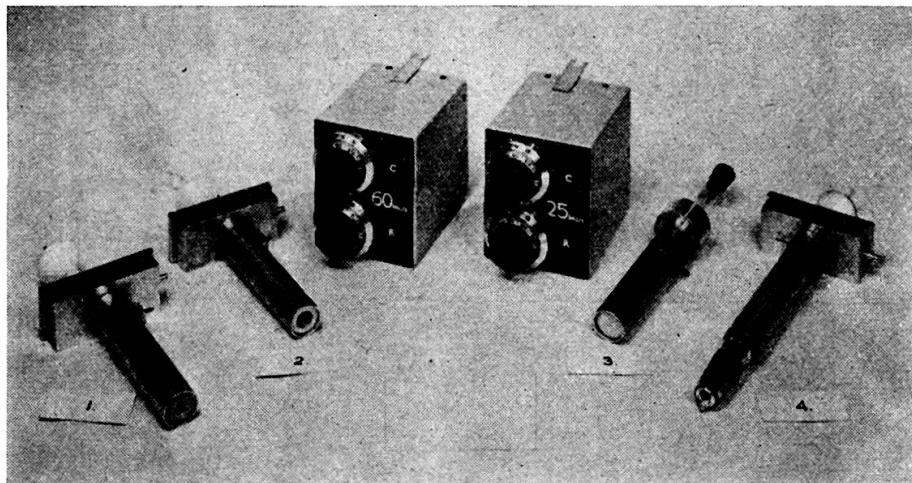


Fig. 4.

Two preamplifier boxes and a range of inserts, (i) 4.5 mm o.d. spinning tube, (ii) 9.0 mm o.d. spinning tube, (iii) 15.0 mm o.d. non-spinning tube and (iv) variable temperature insert for a 4.5 mm o.d. spinning tube.

their axes coincide with the centre of the sample coil and (ii) the best position in the field can be found first and then the final adjustment for homogeneity made in this position.

3.5. *Temperature Variation.*

For work at different temperatures a Dewar system has been found essential to prevent excessive heating of the probe unit or magnet pole shoes and to produce maximum efficiency of heat transfer from the heater to the sample. After removal of a small plate at the bottom of the probe the Dewar insert is pushed into the probe block in the same way as for the other inserts. Figure 5 shows a cross section of the insert and heater in the probe block. Temperatures up to 250° C have been obtained with the prototype with maximum power dissipation of about 75 W in the

heater. An example of its use is illustrated in figure 6 which shows the collapse of the fine structure due to the hindered rotation of the two ethyl groups in diethyl nitrosamine with increase in temperature.

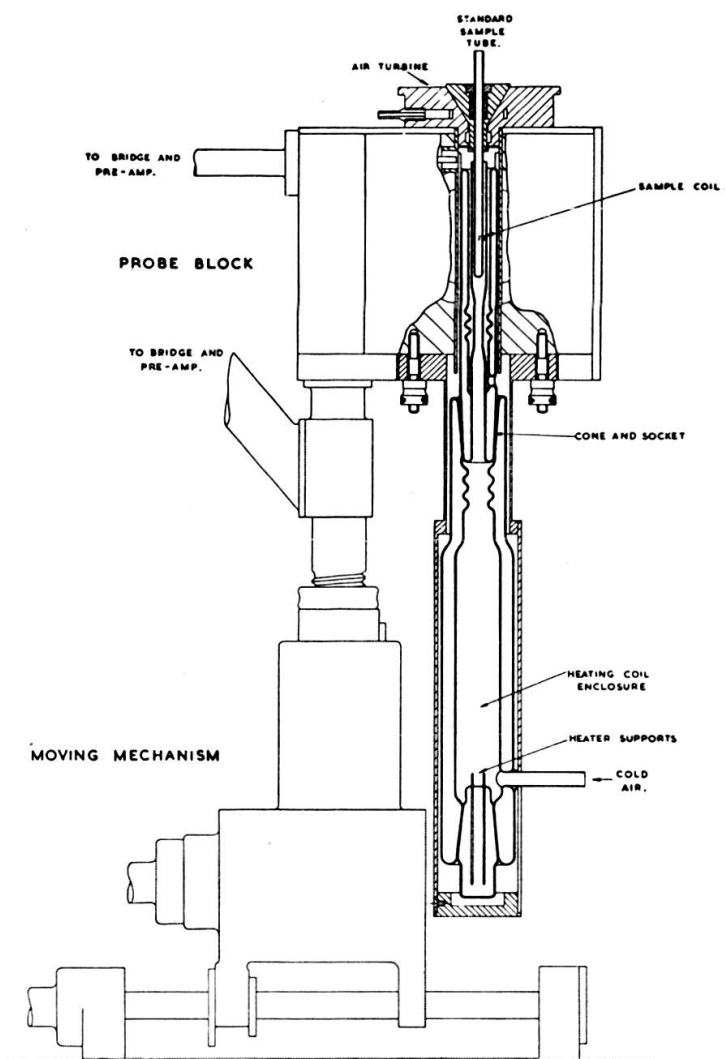


Fig. 5.

Partially sectioned drawing of the probe unit with the variable temperature insert in position.

3.6. R.F. Circuitry.

A block diagram of the r.f. circuitry is shown in figure 7 (a). A wide range of frequencies can be obtained by multiplication of the basic frequency of 2.5 Mc/s provided by the crystal unit. This is a conventional thermostatically controlled crystal unit which has a stability better than 1

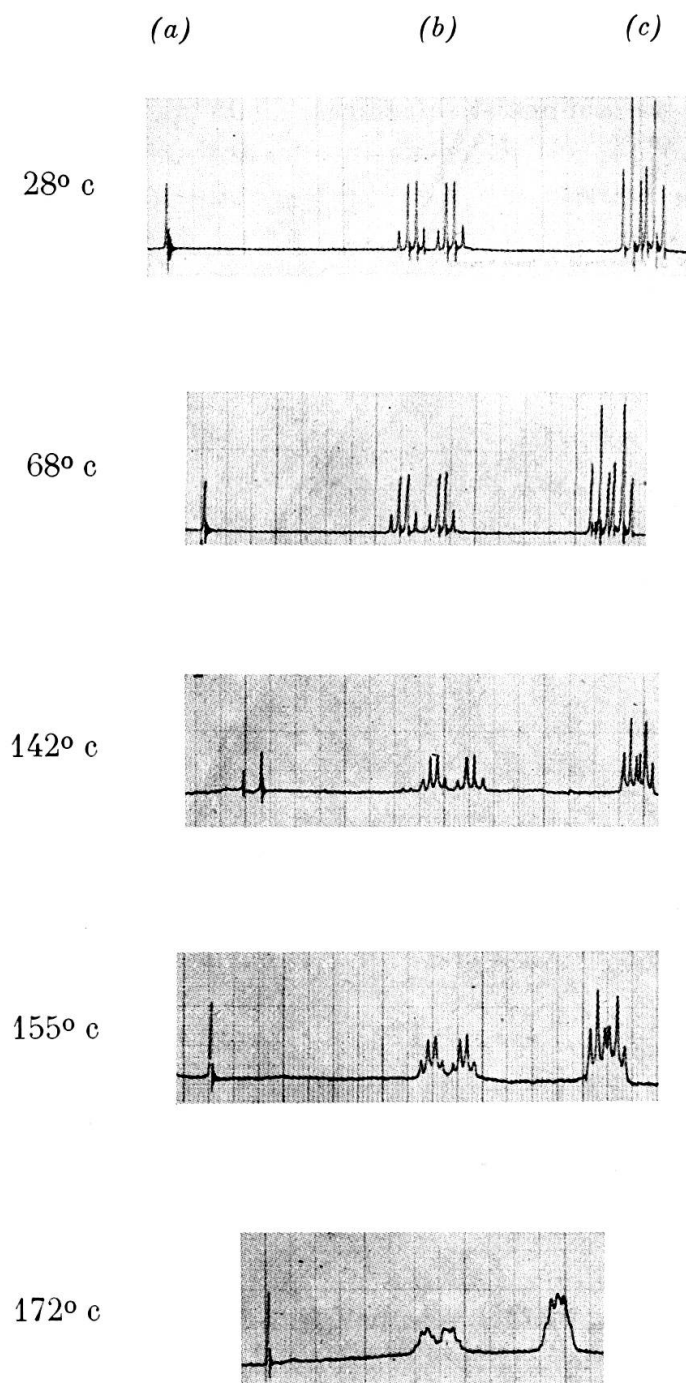
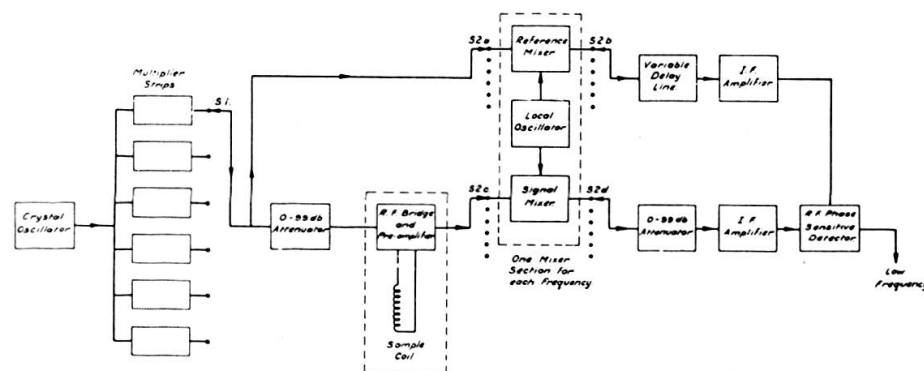


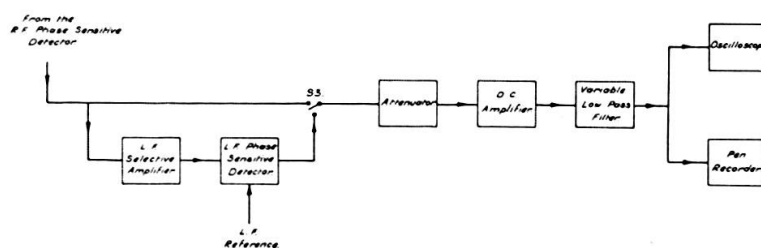
Fig. 6.

60 Mc/s spectra of diethylnitrosamine, $\begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix} \text{N} - \text{N} = \text{O}$
 at different temperatures, (a) benzene capillary as reference, (b) the two CH_2
 groups and (c) the two CH_3 groups.

part in 10^8 per minute. A separate multiplication channel is used for each frequency and this is selected by a co-axial switch S1. The twin-T bridge and pre-amplifier, which are mounted on the probe assembly, are followed by a superheterodyne receiver and r.f. phase sensitive detector. A common i.f. is used in the receiver for all frequencies and is obtained



(a) R. F. SYSTEM.



(b) L. F. AND RECORDING SYSTEM.

Fig. 7.

Block diagram of the r.f. and the l.f. sections.

by selection of the appropriate mixer channel with the co-axial switch S2. In practice the bridge is brought as close as possible to balance and the absorption or dispersion signal selected by adjustment of a delay line in the reference channel to the phase sensitive detector.

With only six frequencies, namely, 2.5, 5.0, 10.0, 15.0, 25 and 60 Mc/s, it is possible to observe more than 90% of the nuclei in the optimum high field range of 10,000 — 16,000 gauss. The change from one frequency to another is made by simply operating two-coaxial switches, changing the pre-amplifier « box », the sample insert and the value of the magnetic field.

Low frequency amplitude modulation of the r.f. is introduced at the last stage of each of the multiplier chains. This has overcome the difficulty of applying sufficient power to the Helmholtz coils to produce observable sidebands at frequencies greater than about 2 Kc/s. In this way sidebands with separations of up to 50 Kc/s can be observed and used to calibrate directly the large chemical shifts associated with nuclei other than hydrogen.

The position and method of introducing the «lock-in detector» can be seen in the block diagram of the low frequency and recording system shown in figure 7 (b). It consists of a low frequency selective amplifier operating at 18, 73 or 212 c/s, followed by a low frequency phase sensitive detector. A preliminary plot of the derivative of the absorption signal of D_2O is shown in figure 8 at a field of 15,300 gauss (D at 10 Mc/s.). The



Fig. 8.

An example of the derivative of an absorption signal using the lock-in-detector, namely that of D in D_2O .

spectrum was observed using a 15 mm o.d. sample tube, 18 c/s field modulation and an r.f. field of a few milligauss. The line width is about 18 c/s or 1.8 p.p.m., due mainly to field inhomogeneities, as line widths of D_2O in a 4.5 mm o.d. sample tube of 1 c/s or 0.1 p.p.m. have been observed at this field.

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