Instruction Manual
for
MODEL R-24A
NUCLEAR MAGNETIC RESONANCE SPECTROMETER

High Resolution NMR spectrometer.
Model R-24A
220 V 50 c/s. Brevet n° n° 3 641223.
MFG n° 03-4 10-74
Hitachi, Ltd Tokyo, Japan

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N-5301E

PERKIN-ELMER

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DESCRIPTION OF WARRANTY-MODEL R-24A

The Perkin-Elmer Model R-24A NMR is a high precision scientific instrument manufactured to close tolerances and consisting of only high quality components. The sale price of the R-24A includes a standard one-year warranty against defects in workmanship and materials. The warranty period commences at the time of delivery of the R-24A to the FOB point.

To assure stable and high performance, the environment in which the R-24A is installed should be as refined as possible. Although the R-24A features double thermostatting and double magnet shielding, it is important that the instrument be installed in an area free of moving metal objects and temperature fluctuations in excess of specifications.

Routine maintenance, such as probe cleaning and spinner air pump servicing is the responsibility of the user. Should readjustment of the homogeneity coils be required after probe servicing, the user is instructed to consult the Operators Manual and follow the procedure given there. If assistance from a Perkin-Elmer service engineer is required for probe cleaning and readjustment of the homogeneity coils, this will be provided at the standard rate of charge for service.

Modification, or alteration of any mechanical or electrical components, by anyone other than an authorized Perkin-Elmer service engineer, will void the warranty. The user is cautioned to consult the Operators Manual before making any adjustments.

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R-24A CONDENSED OPERATING INSTRUCTION

A. "ZEROING" TMS

(1) Turn recorder power switch to ON.

(2) Adjust turbine position of the 5% TMS sample tube and put sample tube in sample holder and close lid.

(3) Press the 600 Hz SHIFT button, set AMPLITUDE to 7 and press the three NOR (red) buttons.

(4) Operate rapid sweep control so that pen is located on 10 ppm line.

(5) Turn TMS POSITION to the right or left and note TMS peak position by pen movement. Adjust until on 10 ppm line.

(6) Release 600 Hz SHIFT button (putting TMS back to the 0 ppm line).

B. RUNNING SAMPLE

(7) Introduce measurement sample, press SET button and read signal amplitude on the meter.

(8) Set AMPLITUDE to match the meter indication and push NOR mode button.

(9) If TMS is the reference, check position of the TMS peak on 10 ppm line as in step A, (3) to (5). Start sweep by turning recorder NOR SWEEP control to F (forward).

C. RECORDING INTEGRALS

(10) Return the pen and press INT button.

(11) Adjust INTEGRAL BALANCE so that there is no drift after releasing the INT CANCEL button.

(12) Turn recorder NOR SWEEP control to F to start recording.

D. SCALE EXPANSION

(13) Return the pen and press SCALE EXP button.

(14) Set AMPLITUDE to 2 or 3 steps higher than meter indicated for NOR sweep-width used.

(15) Turn recorder NOR SWEEP Control to F to start recording.

1. INTRODUCTION

1.1 GENERAL

During the last decade Nuclear Magnetic Resonance (NMR) Spectroscopy has been applied to an ever-increasing extent to the solution of chemical problems. NMR spectra often yield information that is complementary to data derived from other spectroscopic techniques and, in addition, information that may be unobtainable by any other physical or chemical method.

It is not within the scope of this manual to give a description of the NMR phenomenon itself, but such information may readily be obtained by referring to one of the excellent books available which discuss both theoretical and practical aspects of NMR Spectroscopy in detail. A partial list of books is given below:

Useful references for NMR:

(1) F.A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969 (Elementary picture of NMR).

(2) J.R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Inc., 1965 (Outlines applications).

(3) R.M. Silverstein & G. C. Bassler, "Spectroscopic Identification of Organic Compounds", J. Wiley & Sons, Inc., New York, New York, 1964.

(4) R. H. Bible, Jr., "Interpretation of NMR Spectra. An Emperical Approach", Plenum Press, New York N.Y., 1965. (Non-computer analysis of spectra to obtain coupling constants and chemical shifts.)

(5) E.D.Becker, "High Resolution NMR", Academic Press, New York, New York, 1969.

(6) J.W. Emsley, J.Feeney, L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergammon Press Ltd., Oxford, 1966. (Most comprehensive for theory and references).

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FIGURE 1 OVERALL VIEW OF THE R-24A SYSTEM

1.2 INSTALLATION

1.2.1 LOCATION

The distance of the console from surrounding walls can be minimized to less than 4 in. (10 cm); however, more than 16 in. (40 cm.) is recommended for easier installation. The environmental requirements of the equipment are as follows:

Floor	Capable of withstanding load of 60 lb./ft. (250 Kg/m^2).
Power Supply	100, 115, 200, 220 or 240V single phase, 50Hz or 60 Hz.
Magnetic Environment	In general the site should not be closer than 15 feet (4.5 m.) to places where large ferrous or magnetized objects are handled. Small hand tools moved beyond 2 feet (0.6m) from the magnet box produce no serious effect on the instrument performance. Most laboratory locations are satisfactory, but if the instrument is to be operated very near large electromagnets where the field is constantly changing, or where large magnetized objects are constantly moving, the Service Department should be consulted.
Thermal Environment	Permissible ambient temperature range 16 to 30°C. Maximum rate of change not greater than 2°C per hour and maximum change for 24 hours not greater than 10°C. Draughts from doors or windows and direct sunlight should be prevented from reaching console.

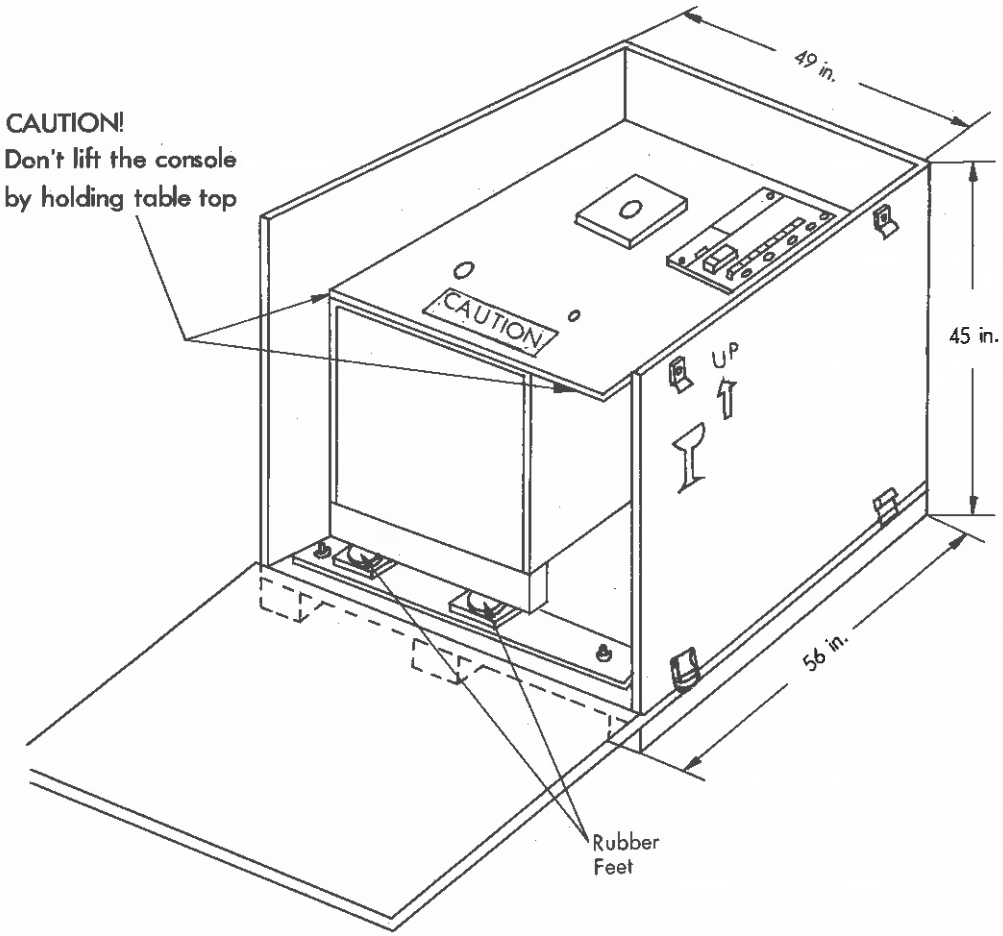
1.2.2 UNPACKING

The cases containing the instrument should be carefully examined for damage upon receipt; if there is any doubt as to the condition of their contents the nearest Service Department should be informed.

CAUTION

The customer should on no account investigate apparent damage. The instrument cases should be carefully stored until the arrival of the Company Representative.

To remove the instrument from its packing crate, open the sides and top of the box. Unfasten the center bolt of each of the four rubber cushions, and lift the instrument by the bottom edges- DO NOT TRY TO LIFT BY THE TABLE TOP.



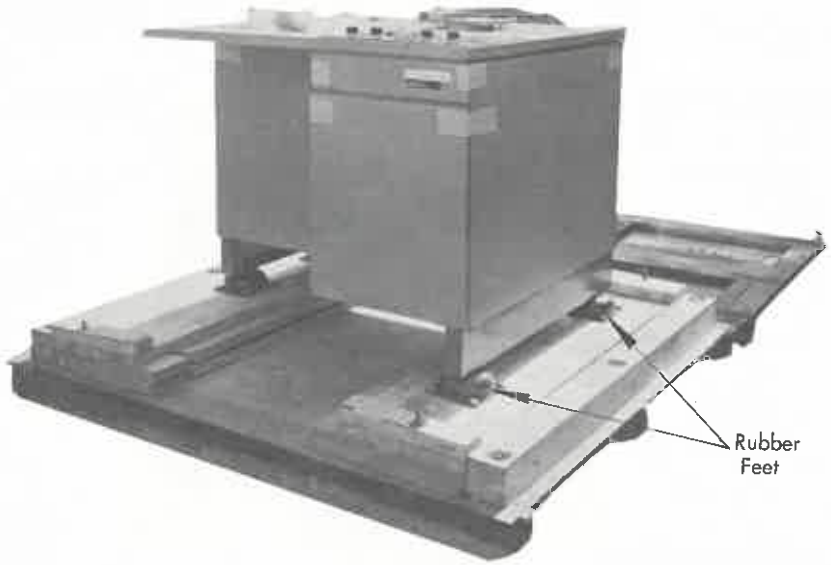


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FIGURE 2 UNPACKING THE R-24A

1.2.3 INITIAL SETUP

It is probably best to perform items (a) to (e) in the afternoon and do (f) the next morning. Letting it stand overnight will facilitate performing the checks and tests.

(a) Place the recorder on the console table and connect cables as shown in figures 3a and 3b. On the back of the recorder are two sets of terminal connections. One has fifteen connections-the other has two.

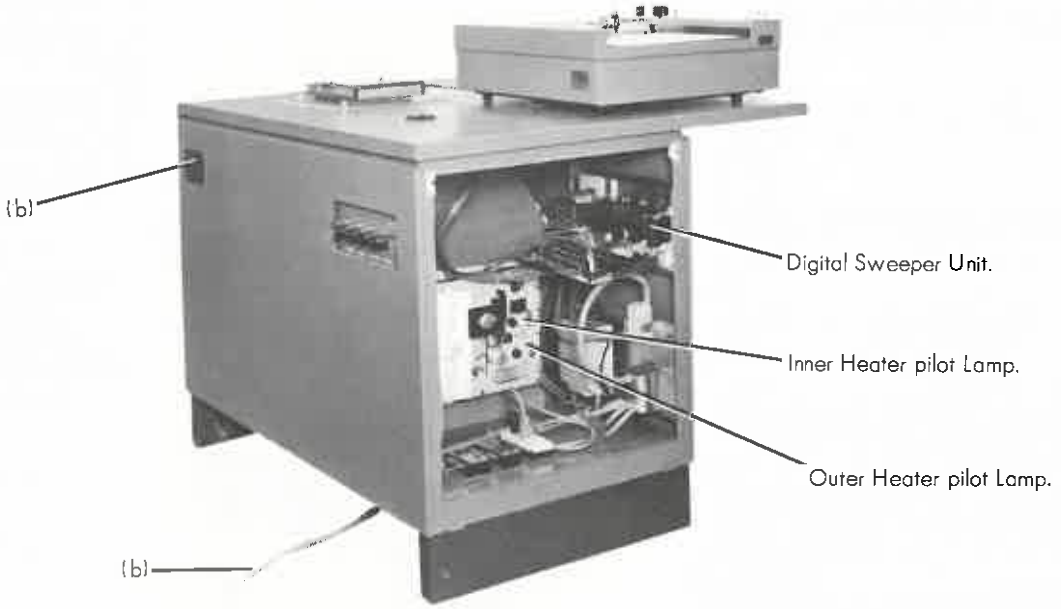

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FIGURE 3a INITIAL SETUP

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FIGURE 3b RECORDER CONNECTIONS

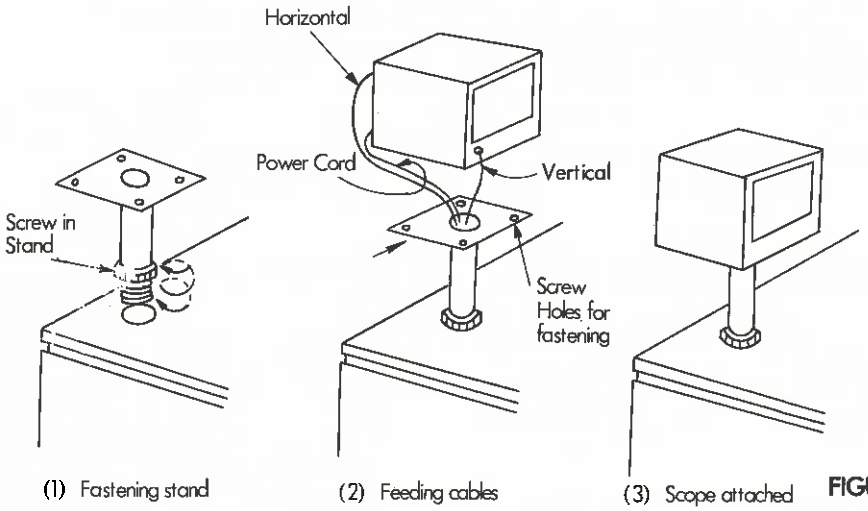


FIGURE 4 CONNECTING THE OSCILLOSCOPE

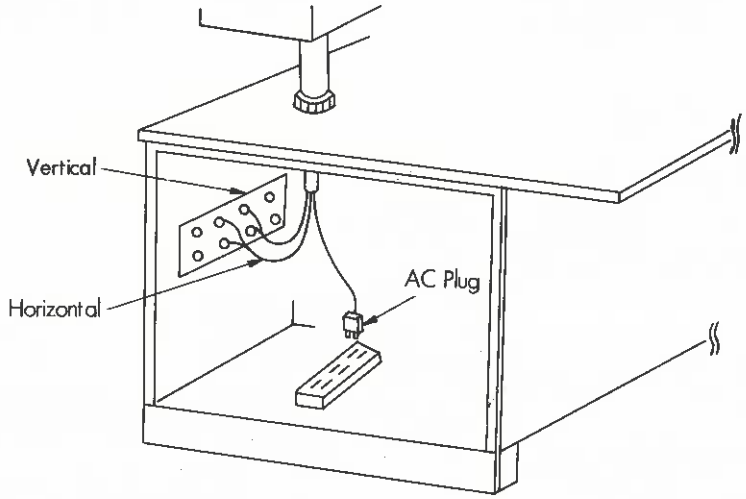


FIGURE 5 CONNECTIONS OF OSCILLOSCOPE IN CONSOLE

(b) The power plug is three-way and check the voltage selector in the console and the correct setting of your power supply.*

(c) Fastening the oscilloscope (See figures 4 and 5) : Screw the oscilloscope stand into the top back left opening of the console. Feed the three cables through the center of the stand and metal plate. Connect the three cables to the oscilloscope terminals-vertical, horizontal and AC power cord. The oscilloscope is fastened to the plate by means of the four screws on the bottom of the unit. Open the left side panel door of the console. A circuit board and a power outlet can be seen at the back of the opening. Connect the other end of the three cables in the left side of the console (Figure 5) to the respective horizontal and vertical terminals on the back of the console and the AC plug to the outlet on the bottom of the console.

(d) The low humming sound of the two air compressors may be heard. Two lighted pilot lamps may be seen, which means that the inner and outer magnet thermostats are in operation.

(e) After a proper length of time (not over a day though it depends on the room temperature), periodic turning on and off of the two small lamps show the inner and outer thermostats are operating at desirable temperatures.

(f) After two days have elapsed from the initial power connection, the magnet should have warmed up so that the TMS-Chloroform sample could be put in the probe and the spectrum will be near the middle of the shift controls and homogeneity check and performance tests can be started as described in later sections (section 4).

(g) If a signal cannot be found it may be necessary to rotate the wide-sweep control behind the hinged front panel to find the correct field for a signal. The signal should be found with the recorder as follows:

(i) Press the three red NOR buttons (figure 6).

(ii) Turn the AMPLITUDE to about 10 (figure 6).

(iii) Set the recorder POWER switch to ON (figure 7).

(iv) Rotate the wide-sweep control (located behind the front right hinged panel) to find the signal which may be seen as a pen deflection.

(v) Position the signal (the USB in figure 9) on the recorder.

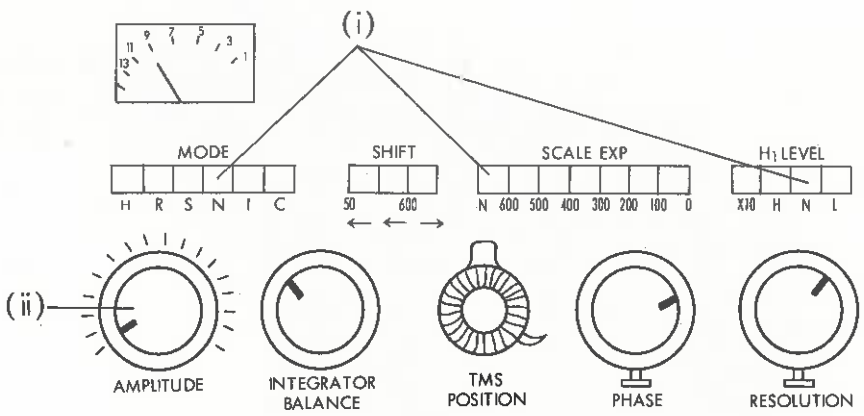


FIGURE 6 CONTROLS FOR LOCATING A SIGNAL.
(Numbers refer to paragraphs in section 1.2.3 (g)).

2. DESCRIPTION OF THE MODEL R-24A

2.1 SCOPE OF THE MODEL R-24A

The magnetic field in the R-24A is very stable, so the high resolution needed for routine analysis can be obtained from the instrument for long periods without adjustment, and accurate reproducible spectra can be run under routine conditions. The baselines of spectra obtained with the instrument are very stable so that integrals may be accurately reproduced.

The applications of the NMR technique are too varied to be discussed in any detail here. It is perhaps useful to list some of the more important fields to which NMR has been applied that may be studied with the R-24A.

(i) General problems of structural analysis in organic chemistry that are often resolvable from measurements of chemical shifts and spin-spin coupling constants.

(ii) Investigations of restricted internal rotation and measurement of potential energy barriers.

(iii) The study of reaction kinetics and mechanism and in particular of proton exchange effects e.g. useful work has been done in the examination of chemical equilibria such as the keto-enol tautomerism.

(iv) Examination on specific molecular interactions in the liquid phase, and in particular of hydrogen bonding effects.

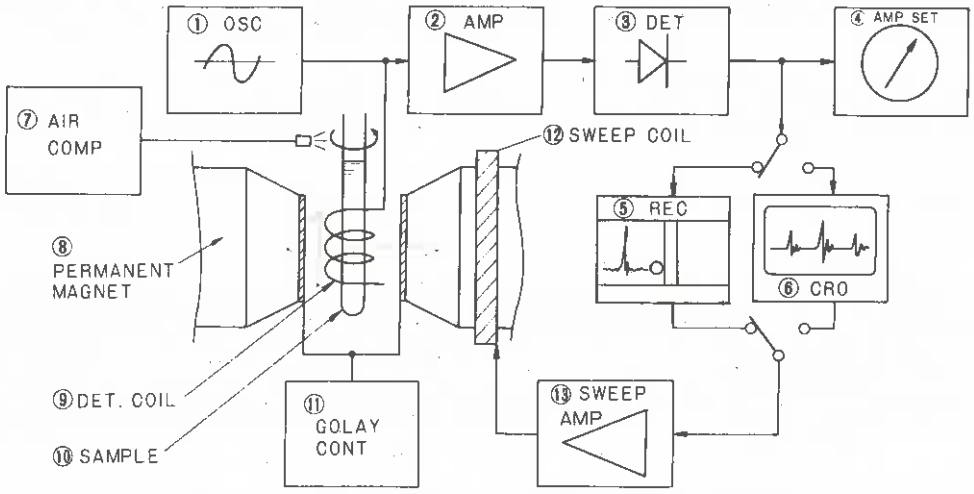
(v) Quantitative analysis of simple mixtures.

2.2 SYSTEM DESCRIPTION

Control of the magnet temperature is achieved by placing the magnet in thermostatically controlled enclosures. The field stability achieved by means of the double oven around the magnet is such that short-term variations are almost eliminated and longterm field drift is reduced to a very low level. To obtain high resolution (i.e. narrow peaks) from the instrument, it is essential that the homogeneity of the magnetic field around the sample irradiation region be very good. If the field affecting the nuclei in different parts of the sample varies, a broadening of the lines occurs with resultant loss of resolution so that fine splittings cannot be observed. To improve field homogeneity, nine pairs of Golay coils are fitted between the pole faces. The currents through these coils can be varied individually to produce small changes in the field flux distribution. To reduce the effect on the resolution of any residual field variation, the sample tube is spun about its axis during analysis. Sample spinning causes the horizontal inhomogeneities in the field to be averaged to near zero, simplifying the field correction required. Sweep and shift coils are wound on one of the magnet poles of the magnet assembly. To scan the spectrum, the magnet field is swept through a small range by passing a small sawtooth current through the sweep coils. The sweep width may be varied by changing the amplitude of the sawtooth. The sweep position in the field may be varied by changing the current intensity. The sweep voltage for the sweep coils and the recorder are obtained from digital sweeper unit therefore the position of the spectral information corresponds to the field scan.

The sweep width selected for study is varied by depressing scale expansion push buttons, which change the sweep voltage amplitude on the coils.

The 60 MHz irradiation field is obtained from a crystal-controlled oscillator assembly contained in a temperature regulated container. The short-term stability of the oscillator is 5 parts in 10^9 or better. A 15kHz signal, also obtained from a crystal-controlled oscillator, is applied to coils orthogonal to the probe r.f. coil and aligned with the magnet axis, so that the magnet field in the sample region is audio-frequency modulated. At resonance the sample acts as a mixing device and NMR sidebands are pro-



① Crystal-controlled oscillator (60 MHz)
② Low Noise Radio-frequency Amplifier
③ Phase Detector
④ Amplitude Setting Circuit
⑤ Recorder
⑥ Cathode-ray Oscilloscope
⑦ Air Compressor for Sample Spinning
⑧ Permanent Magnet
⑨ Signal Detector Coil
⑩ Sample Tube
⑪ Golay Control
⑫ Sweep Coil
⑬ Sweep Amplifier

FIGURE 10 BLOCK DIAGRAM OF THE R-24A

duced at field strengths corresponding to 59.985 and 60.015 MHz. Each sideband induces in the probe a 60 MHz radio frequency response, amplitude modulated at 15 kHz (the phase relationship of the modulation containing information corresponding to the absorption and dispersion components of the NMR signal).

The probe output is applied to the sample, inducing the resonance signal which is detected to obtain the 15 kHz signal; this signal is amplified, and compared in phase with the reference signal of adjustable phase derived from the 15 kHz oscillator.

The reference phase is adjusted using the PHASE control so that the absorption component of the upper (60.015 MHz) sideband is recorded. As there is no output from the r.f. amplifier in the absence of the resonance, the spectrum baseline is extremely stable.

The baseline is automatically shifted on the recorder chart depending on the mode of operation, normal, integral and scale expansion. The integrator circuit is in operation when INT button is pushed. When the spectrum is being integrated, a measurement of the total area equivalent to each of the peaks in the spectrum is recorded.

2.3 FUNCTION OF CONTROLS

2.3.1 CONTROLS ON THE RECORDER

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FIGURE 11 RECORDER CONTROLS

(a) POWER : ON/OFF

Switch for turning on and off the power to the recorder. When this switch is turned off, the recorder is disconnected from the power supply, and when turned on, power is applied with the pilot lamp lit.

(b) CHART : HOLD/FREE

Switch for holding the chart. When this is set to HOLD, the chart is held. When it is set to FREE, the chart is released.

(c) PEN : DOWN/UP/AUTO

Switch for lifting and lowering the recorder pen.

DOWN : The pen lowers both in RAPID SWEEP and NOR SWEEP modes.

UP : The pen lifts both in RAPID SWEEP and NOR SWEEP modes.

AUTO : The pen lifts over the entire range in RAPID SWEEP mode, and automatically lifts or lowers at the start and end points in NOR SWEEP mode.

(d) SWEEP MODE

RAPID ; B←/→F

This rapid sweep switch permits sweeping the chart in either backward or forward direction according to setting.

NOR : B←/→F

Switch for setting the sweep direction. This permits sweeping the chart in either forward or backward direction according to setting.

Set this switch always at the center while the pen is stopped.

(e) SWEEP TIME

Switch for setting the sweep time.

The sweep time of R-24A is 300 sec. in ordinary measurements and automatically set to 150 sec. in integral measurements with the INT button depressed.

(f) ZERO SHIFT

Knob for optionally shifting the recorder pen position on the Y-axis.

It is set to the 10 % line of the full scale in ordinary measurements.

(g) ZERO CHECK

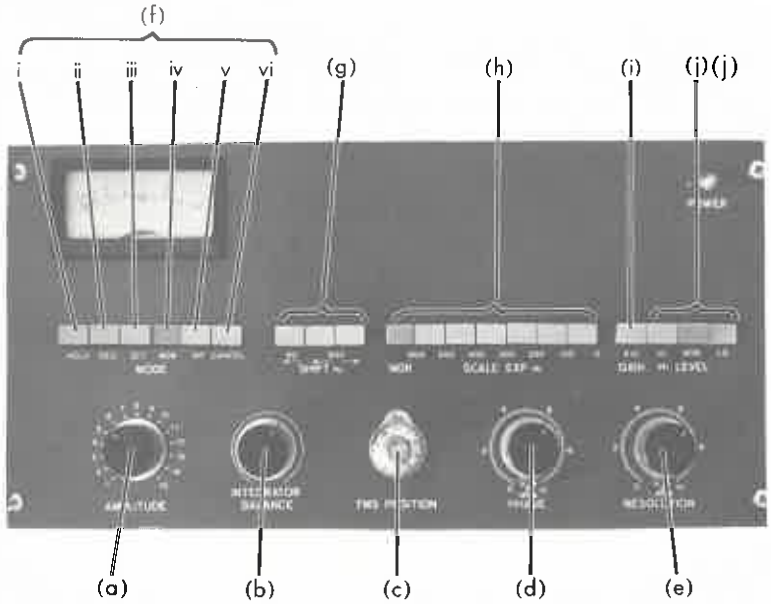
Switch for checking the zero point on the Y-axis.

(h) CHART ZERO

This scale is used for determining the chart position.

Hold the chart by setting the ↓ mark on the chart to this scale.

(See section 2.3.2)



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(Letters refer to description paragraph in section 2.3.2)

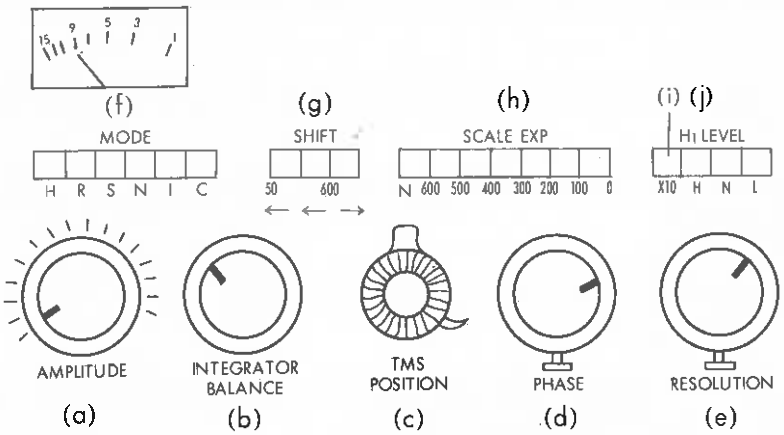


FIGURE 12 CONTROLS ON THE MAIN PANEL

2.3.2 CONTROLS ON THE MAIN PANEL (See figure 12 on the fold-out previous page)

The following descriptions of control functions are arranged in order as the controls are located on the panel left to right.

(a) AMPLITUDE

The sensitivity of the recording system and therefore the observed peak amplitudes are increased in fifteen binary steps as this control is turned from the extreme left to the extreme right. The switch positions are arbitrarily numbered 1 to 15; the amplitude increments are 1.4:1 (See section 5.5 for routine AMPLITUDE selection).

(b) INTEGRATOR BALANCE

The integrator balance control is adjusted to obtain a level integral baseline; it is adjusted so that any small d.c. output from the Phase Detector, remaining when there is no NMR signal is cancelled (See section 5.6 for routine adjustment of the INTEGRATOR BALANCE).

(c) TMS POSITION

A continuous shift of the spectrum of 1000 Hz may be obtained by adjusting the TMS POSITION control; it is calibrated in Hz.

(d) PHASE

The PHASE control, which may be rotated continuously, is adjusted to select the absorption mode signal. It seldom needs adjustment, except when changing between solvents with very different dielectric constant. Setting the PHASE is described in sections 3.1 and 5.6.

(e) RESOLUTION

Fine adjustment of the instrument resolution may be made with this control (see section 5.4 for routine and section 3.1 for major adjustments of resolution).

(f) MODE PUSHBUTTONS

There are six pushbuttons for mode control.

(i) HOLD

By pressing this pushbutton when the recorder pen is positioned on a resonance peak, the control loop is closed so that the NMR signal position is maintained. No signal is obtained on the recorder in this condition.

The check meter reading reflects the change in the field position which has been corrected since the lock button was pressed.

(ii) RES

The amplitude of a peak may be measured on the check meter by pushing this button when the recorder pen is located on the peak. The resolution can then be readjusted with the RESOLUTION knob for a maximum needle deflection to the right on the meter. Use of the RES is described in section 3.1.

(iii) SET

The maximum peak amplitude of the spectral lines for the sample is indicated on the meter after pressing this button. The scan takes 7 seconds. The meter scale is graduated from 1 to 15 which corresponds to the suggested setting of the AMPLITUDE control for a full-scale spectral display. Use of the SET button is described in section 5.5.

(iv) NOR (red)

Normal spectra may be recorded when this button is pressed.

(v) INT

When this pushbutton is pressed the integrator is turned on and the sweep speed of the recorder is doubled. Use of the INT is described in Section 5.6.

(vi) CANCEL

Pressing the integral CANCEL button removes the accumulated integral, and returns the pen to the integral baseline position.

(g) SHIFT

The magnetic field may be shifted 50 or 600Hz by depressing the SHIFT buttons. The field strength is increased or decreased and the recorded peaks shifted in the direction shown by the arrows under the numbers.

(h) SCALE EXP.

The width of the spectrum recorded may be changed by pressing the SCALE EXP. buttons. A normal 10 ppm (600 Hz) spectrum width is obtained by pressing the red NOR button. Use of the SCALE EXP. is described in section 5.7 . The other six buttons correspond to portions of the 600 Hz range, each button covering a 100 Hz sweep width with its relative portion of the 600 Hz range shown in Hz. One or more buttons can be pressed at the same time to obtain the desired sweep width in multiples of 100 Hz.

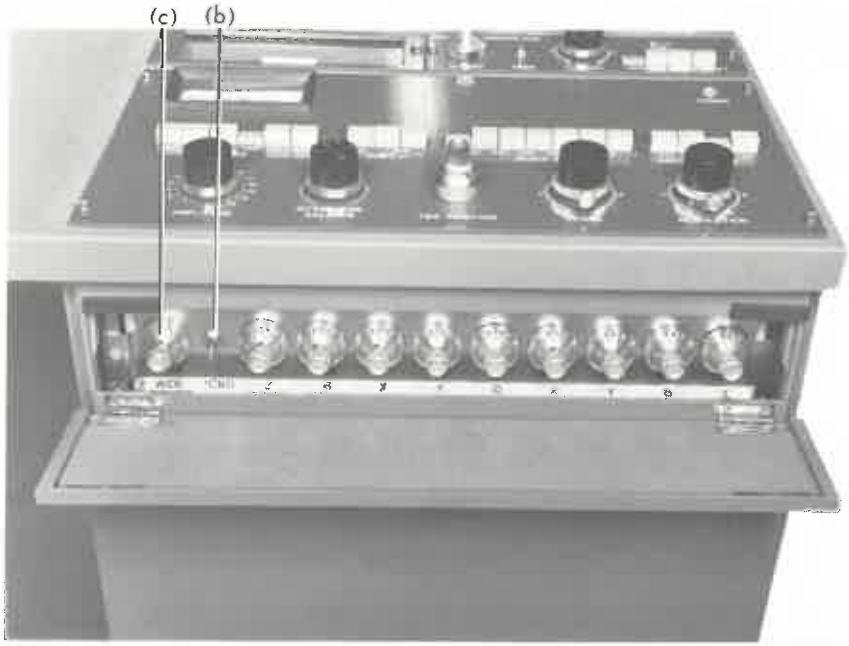
(i) GAIN X10

The gain of the signal amplifier is multiplied by a factor of ten by pressing the GAIN X 10 button. This also provides greater levels of baseline-noise damping in the circuit. Use of the GAIN X10 is described in section 5.5.

(j) H_1 LEVEL

The r.f. irradiating power may be selected by pressing the HI, NOR or LO button. For a neat sample, the LO level is desirable. For a solution between 50% and 5% sample concentration the NOR level (and perhaps with lower concentrations the GAIN X10) should be used.

(See section 2.3.3)



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(Letters refer to description paragraph in Section 2.3.3)

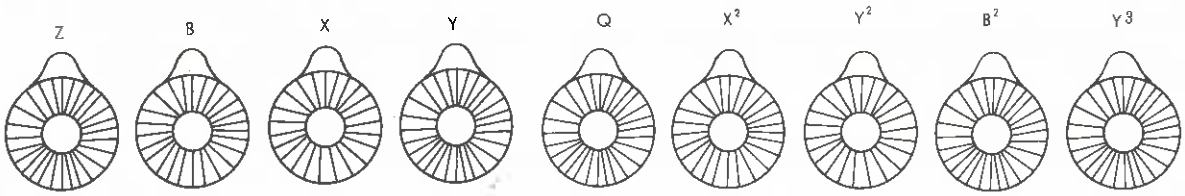

FIGURE 13 CONTROLS BEHIND HINGED PANEL

The HI setting is used with dilute samples (less than 5% concentration.)

2.3.3 CONTROLS BEHIND HINGED PANEL (See fold-out figure 13)

(a) GOLAY CONTROLS

Behind the hinged panel beneath the main control panel of the console are located nine Golay control potentiometers which adjust the homogeneity of the permanent magnet field. These controls do not require frequent adjustment and should normally be locked. To adjust them see section 3.1.

(b) CRO/REC SWITCH

A cathode-ray oscilloscope can be used to make survey scans and to adjust the resolution. Selection of either the scope observation or recorder mode is made with the CRO/REC SWITCH.

(c) WIDE SHIFT

The magnet field may be shifted by rotating the WIDE SHIFT knob. It has a range of approximately 50 ppm (3000 Hz). This potentiometer should be kept locked except when in use.

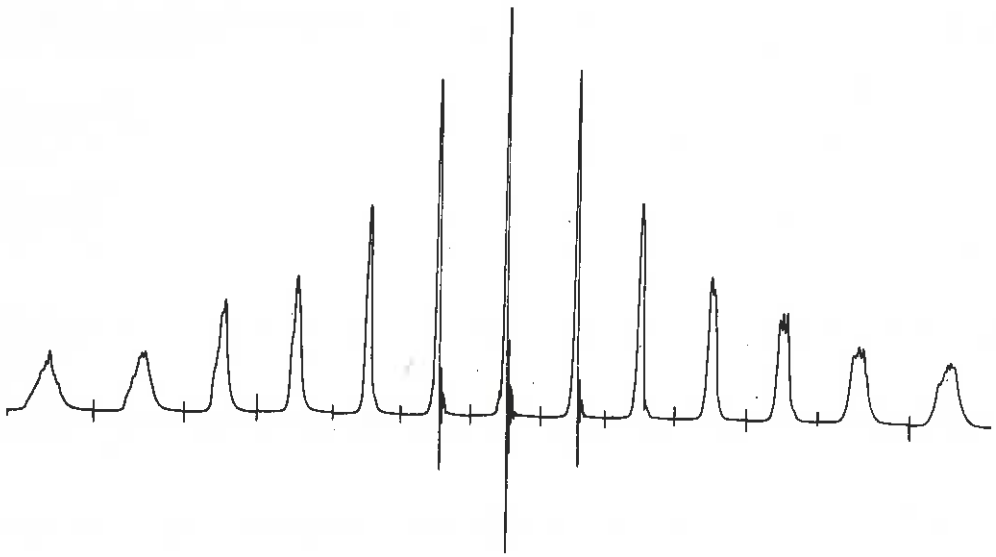

FIGURE 14 EFFECT OF CHANGING THE RESOLUTION CONTROL IN STEPS ON A TMS SIGNAL