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The Probehead
Part g1

The Probehead

Function, Structure and Overview

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Chapter 1

Introduction

In general, two groups of probes are discriminated because of their widely different design principles: these are high resolution probes (manufactured in Zurich) and high power probes (manufactured in Karlsruhe). High resolution probes are designed to provide ease of handling, best possible lineshape, resolution and sensitivity, whereas high power probes are optimized for short pulse width, short dead time and wide bandwidth (not to be confused with wide tuning range). These requirements are different from the requirements for HR probes and necessitate very different design principles.

In this manual we will break the probes down further into three groups . These will be high resolution, high power and imaging / diffusion (those requiring gradient coils). In chapter 2 all probes will be discussed with the later chapters handling each group individually.

Chapter 2

Probe Types Available

Considering the range of magnets, sample sizes, and tuning ranges, it becomes obvious that far more than several hundred probes must be produced, not counting the numerous special probes. There are, however, many features common to all probes which makes classification quite simple. There is also a range of modifications to standard probes available to tailor probes to the customer's specific requests.

This chapter provides an overview of the various types of probeheads that are available for high resolution as well as high power systems and shows what can be measured with them.

2.1 High Resolution Probes

When ordering high resolution probes the following "code" should be used: M-F-O-D-L-S-T

M: Magnet type (SB,WB)
F: Basic NMR frequency in MHz
O: Observe nucleus (if double tuned or on 2 coils: separate both nucleus by "/")
D: Decoupling (if double tuned: separate both nucleus by "/")
L: Lock
S: Sample diameter
T: Special types (QNP,HT,CIDNP,MAS,MICROIMAG)

Examples:

1. Standard dual probe :WB-300-13C/1H-1H-2H-05
2. Inverse probe :SB-500-1H-13C/1H-2H-05
3. Multinuclear low range :SB-600-BBLR-1H-2H-10
4. QNP probe :SB-400-1H/19F/31P/13C-1H-2H-05-QNP

The temperature range of these probeheads is as follows:

1. **Probes with 5mm sample diameter:**	$^{-}150^{\circ}$ - $^{+}180^{\circ}$ C
2. **Probes with 10mm sample diameter:**	$^{-}130^{\circ}$ - $^{+}150^{\circ}$ C
3. **Probes with 15 & 20mm sample diameter:**	$^{-}80^{\circ}$ - $^{+}120^{\circ}$ C
4. **VT/MAS probes:**	$^{-}100^{\circ}$ - $^{+}150^{\circ}$ C

Any exceptions are specially noted.

2.1.1 Selective Probeheads

With this probehead, the observe channel (inside coil) is tuned to a particular resonance frequency. The decoupling channel (outside coil) is tuned for ^{1}H.

^{1}H Selective

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	Homodecoupling	^{2}H	5	100,200,250,300, 360,400,500,600	tunable to ^{19}F (250,300,360, 400 & 500 MHz)

^{19}F Selective

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{19}F	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	free of background on ^{19}F
^{19}F	^{1}H	^{2}H	10	100,200,250,300, 360,400,500,600	free of background on ^{19}F

Other nucleus (Selective probeheads)

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{13}C	^{1}H	^{2}H	10	100,200,250,300, 360,400,500,600	Standard probehead.
^{31}P	^{1}H	^{2}H	10	100,200,250,300, 360,400,500,600	High sensitivity.
^{11}B, ^{29}Si, ^{27}Al.	^{1}H	^{2}H	10	100,200,250,300, 360,400,500,600	free of background signal on observe nucleus. temperature range ± 80° C.
^{2}H	^{1}H	^{19}F	10,15	200,250,300, 360,400,500,600	additional hardware required, ^{19}F lock accessory necessary.
^{3}H	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	leak-proof insert, temperature range ± 80° C.

2.1.2 Dual Probeheads

Measurements can be made both on the observe channel and on the decoupling channel.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H and ^{19}F	^{1}H or ^{19}F	^{2}H	5	100,200,250,300, 360,400,500,600	free of background on ^{1}H
^{1}H and ^{13}C	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	Standard probe.
^{1}H and ^{31}P	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	

2.1.3 Double tuned probeheads

The Observe or Decoupling channels can be doubly tuned depending on the application, the lock channel will be placed on either channel.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{31}P and ^{13}C	^{1}H	^{2}H	5,10	100,200,250,300, 360,400,500,600	
^{13}C	^{1}H and ^{31}P	^{2}H	5,10	100,200,250,300, 360,400,500,600	

2.1.4 DPP Probeheads (Dual Pneumatic Probe)

The observe channel can be switched between two resonance frequencies by means of a pneumatic switch. The decoupling channel is tuned to one frequency.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{31}P/^{13}C	^{1}H	^{2}H	10	200,250,300, 360,400,500	switch is controlled by software, additional hardware required
^{31}P/^{13}C	^{1}H	^{2}H	20	200WB,300WB 400WB	as above

2.1.5 QNP Probeheads (Quad Nuclei Probe)

The observe channel can be switched between three resonance frequencies by means of a digital switch. The decoupling channel can be used to measure and to decouple ^1H.

An additional software-driven pneumatic unit can provide fully automatic switch-over. However, this probe is not suited for rapid and frequent switch-over, the DPP probe should be used for this application.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^1H Freq. MHz	Notes—
^1H, ^{19}F, ^{31}P and ^{13}C	^1H	^2H	5	200,250,300, 360,400	Standard probe. switch controlled by software, additional hardware required
^1H, ^{19}F, ^{31}P and ^{13}C	^1H	^2H	5	500,600	Reduced specifications on ^{13}C
^1H, ^{31}P, ^{13}C and ^{15}N	^1H	^2H	5	200,250,300 360,400,500,600	
(^1H), ^{31}P, ^{13}C and ^{15}N	^1H	^2H	10	200,250,300 360,400,500,600	Reduced specifications on ^1H

2.1.6 Multinuclear (BB) Probeheads

By means of digital switches, the observe channel can be set to the various resonance frequencies. Matching is achieved through further digital switches. The decoupling channel is tuned to one frequency.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^1H Freq. MHz	Notes—
BB Range:					
^{31}P - ^{15}N and ^1H	^1H	^2H	5	100,200,250,300, 360,400,500,600	Dual ^1H/BB
^{31}P - ^{109}Ag	^1H	^2H	10	100,200,250,300, 360,400,500,600	Standard probe
^{31}P - ^{109}Ag	^1H	^2H	15	200,250,300 360,400	
^{31}P - ^{109}Ag	^1H	^2H	20	200WB, 300WB, 360WB, 400WB	
^{39}K - ^{41}K	^1H	^2H	10	200,250,300, 360,400,500,600	Low range

2.1.7 Inverse Probeheads

These Probes have ^{1}H and lock channel on the observe channel. The decoupling channel is either tuned for a selective frequency or broadband.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	^{13}C (or ^{31}P or ^{15}N)	^{2}H	5	200,250,300, 360,400,500,600	Standard inverse probe.
^{1}H	Double tuned: ^{31}P and ^{13}C	^{2}H	5	200,250,300 360,400,500,600	
^{1}H	Double tuned: ^{13}C and ^{15}N	^{2}H	5	200,250,300 360,400,500,600	
^{1}H	BB, high range: ^{31}P - ^{109}Ag	^{2}H	5	200,250,300 360,400,500,600	

2.1.8 High-temperature Probeheads

This probe makes it possible to study samples up to a 450° C.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	Homodecoupling	^{2}H	5	200,250,300, 360,400,500	Standard range: $^{+}$10 - $^{+}$450° C Special design up to 600° C
^{19}F	^{1}H	^{2}H	5	200,250,300, 360,400,500	Standard range: $^{+}$10 - $^{+}$450° C Special design up to 600° C
^{13}C	^{1}H	^{2}H	10	200,250,300 360,400,500	Standard range: $^{+}$10 - $^{+}$450° C Special design up to 600° C

2.1.9 CIDNP Probeheads

(CIDNP: Chemical Induced Dynamic Nuclear Polarization)

The substance being investigated can be irradiated with light, via a quartz light pipe, during the experiment.

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	Homodecoupling	^{2}H	5	100,200,250,300, 360,400,500,600	with quartz light pipe Reduced specifications.
^{19}F	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	with quartz light pipe Reduced specifications.
^{13}C and ^{1}H	^{1}H	^{2}H	5	100,200,250,300, 360,400,500,600	with quartz light pipe Reduced specifications.
^{13}C	^{1}H	^{2}H	10	200WB, 300WB, 400WB	with quartz light pipe Reduced specifications.

2.2 Imaging & Diffusion Probeheads

2.2.1 Micro-Imaging Probeheads

Observe nucleus	Decoupling	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	Homodecoupling	$2\frac{1}{2}$,5,10	SB: 100,200,250,300, 360,400,500	With gradient coils and exchangeable inserts.
^{1}H	Homodecoupling	$2\frac{1}{2}$,5,10 15,20,25	200WB, 300WB, 400WB	With gradient coils and exchangeable inserts.
Insert tuned to one X-nucl. within range : ^{31}P - ^{17}O	^{1}H (not with diam. $2\frac{1}{2}$ & 25)	$2\frac{1}{2}$,5,10 15,20,25	200WB, 300WB, 400WB	With gradient coils and exchangeable inserts.

2.2.2 Mini-Imaging Probeheads

Observe nucleus	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H/^{31}P	70	200,300,360,400	Probe doesn't include gradient coils Used on Super Wide Bore magnets
^{19}F	70	200,300	Probe doesn't include gradient coils Used on Super Wide Bore magnets
^{1}H/^{13}C	70	300,400	Probe doesn't include gradient coils Used on Super Wide Bore magnets

2.2.3 Diffusion Probeheads

Observe nucleus	Decoupling	Lock	Dia. (mm)	^{1}H Freq. MHz	Notes—
^{1}H	Homodecoupling	^{2}H	5	100,200,250,300, 360,400,500,600	With Z-gradient for Homospoil or Diffusion. Temp. range : ± 100° C.

2.3 High power probeheads

2.3.1 CP/MAS Probeheads

(CP: Cross Polarization, MAS: Magic Angle Spinning)

This probe is designed for the analysis of solids. The sample rotates along an axis angle of 54°44′ (MAS) at a frequency of 7 kHz for 7mm and 17 kHz for 4mm. The temperature range is $^{-}$100° - $^{+}$120° C. With a high temperature option to $^{+}$230° C.

For the 7mm probeheads there is an option of ^{27}A free air bearings.

(For further data, see Part i1, MSL spectrometer).

Observe nucleus	Decoupling	Dia. (mm)	^{1}H Freq. MHz	Notes—
Range: ^{31}P - ^{15}N	^{1}H (high power)	4 or 7	SB: 300,360 400,500,600	Spinning speed up to 15 (5) kHz
^{31}P - ^{17}O and ^{15}N	^{1}H (high power)	4 or 7	SB: 200,250	Spinning speed up to 15 (5) kHz
CRAMPS	-	7	100WB	Spinning speed up to 5 kHz
^{31}P - ^{29}Si	^{1}H (high power)	7	100WB	Spinning speed up to 5 kHz
CRAMPS	-	7	200WB	Spinning speed up to 5 kHz
^{31}P - ^{29}Si	^{1}H (high power)	7	200WB	Spinning speed up to 5 kHz
^{11}B - ^{15}N	^{1}H (high power)	7	200WB	Spinning speed up to 5 kHz
^{31}P - ^{29}Si	^{1}H (high power)	4	200WB	Spinning speed up to 15 kHz
CRAMPS	-	7	300WB	Spinning speed up to 5 kHz
^{31}P - ^{2}H	^{1}H (high power)	7	300WB	Spinning speed up to 5 kHz
^{2}H - ^{63}Cu	^{1}H (high power)	7	300WB	Spinning speed up to 5 kHz
^{27}Al - ^{15}N	^{1}H (high power)	7	300WB	Spinning speed up to 5 kHz
^{31}P - ^{29}Si	^{1}H (high power)	4	300WB	Spinning speed up to 15 kHz
CRAMPS	-	7	360WB	Spinning speed up to 5 kHz
^{27}Al - ^{17}O	^{1}H (high power)	7	360WB	Spinning speed up to 5 kHz
CRAMPS	-	7	400WB	Spinning speed up to 5 kHz
^{31}P - ^{13}C	^{1}H (high power)	7	400WB	Spinning speed up to 5 kHz
^{27}Al - ^{15}N	^{1}H (high power)	7	400WB	Spinning speed up to 5 kHz
^{31}P - ^{59}Co	^{1}H (high power)	4	400WB	Spinning speed up to 15 kHz
^{27}Al - ^{15}N	^{1}H (high power)	7	500WB	Spinning speed up to 5 kHz
^{31}P - ^{13}C	^{1}H (high power)	4	500WB	Spinning speed up to 15 kHz

2.3.2 High power BB & Fixed freq. probeheads

Observe nucleus	Decoupling	Dia. (mm)	^{1}H Freq. MHz	Notes—
CP Probes:				
^{31}P - ^{13}C	^{1}H (high power)	5 or 7.5	200WB	
^{11}B - ^{15}N	^{1}H (high power)	5 or 7.5	200WB	
^{31}P - ^{2}H	^{1}H (high power)	5 or 7.5	300WB	
^{27}Al - ^{15}N	^{1}H (high power)	5 or 7.5	300WB	
^{11}B - ^{17}O	^{1}H (high power)	7.5	360WB	
^{31}P - ^{13}C	^{1}H (high power)	7.5	400WB	
^{27}Al - ^{15}N	^{1}H (high power)	5 or 7.5	400WB	
Fixed Freq.:				
^{1}H	-	5 sol.	WB: 200,300, 360,400	
^{19}F	-	5 sol.	WB: 200,300, 360,400	
^{109}Ag - ^{31}P	-	10 sat. or sol.	WB: 200,300, 360,400	with switchable inserts, 5mm insert avail. for ^{2}H.
^{2}H - ^{13}C	-	7.5 sol.	WB: 200,300, 360,400	
^{13}C - ^{31}P	-	7.5 sol.	WB: 200,300, 360,400	
^{15}N	-	7.5 sol.	WB: 200,300, 360,400	

2.3.3 High power Low temp. (<20° K) probeheads

Observe nucleus	Dia. (mm)	Notes—
40 MHz	5 or 7.5	Requires low temp. cryogenic accessory.
50 MHz	5 or 7.5	Requires low temp. cryogenic accessory.
70 MHz	5 or 7.5	Requires low temp. cryogenic accessory.
80 MHz	5 or 7.5	Requires low temp. cryogenic accessory.
300 MHz	5 or 7.5	Requires low temp. cryogenic accessory.
400 MHz	5 or 7.5	Requires low temp. cryogenic accessory.

Chapter 3

High Resolution Probes

This chapter briefly explains the generation and reception of NMR signals as well as the basic structure of a probehead.

Furthermore, the system interconnection and the signal path from the probehead to the receiver is described.

3.1 Theory of Operation

In the ground state (figure 1.1), the nuclear spins (i.e. the magnetization vector $\vec{M}$) of the sample are aligned parallel to the principal magnetic field ($\vec{B}_0$ field).

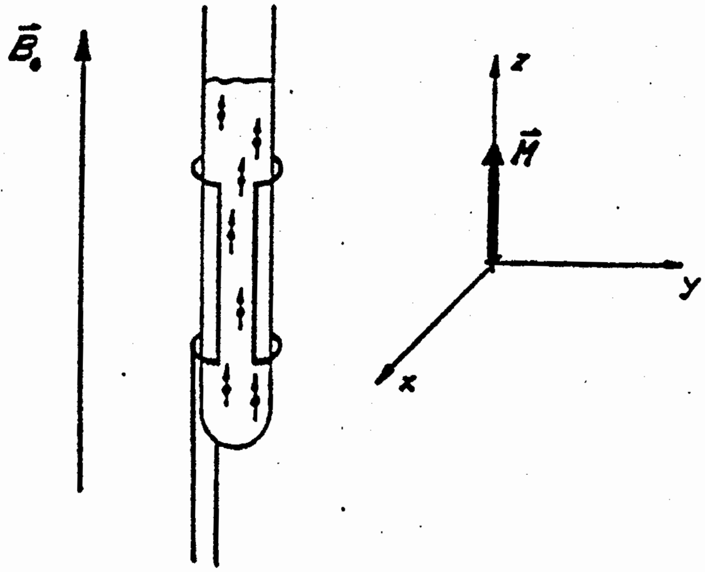

Figure 3.1: Ground State

By applying a rotating magnetic field $\vec{B}_1$ ($f\ \vec{B}_1$ = resonance frequency of the nuclei being measured) the magnetization vector is deflected by an angle ϕ. If $\phi = 90°$, one speaks of a 90° pulse (figure 1.2). ϕ is proportional to the RF field of the coil ($\vec{B}_1$) and to the time (t) during which $\vec{B}_1$ is on ($\phi \alpha \vec{B}_1 t$), i.e. the pulse duration for a particular pulse angle is all the shorter as the magnetic $\vec{B}_1$ is stronger (for further data see Part c3, NMR Physics). $\vec{B}_1$ depends on the quality factor (Q) of the transmit/receive coil and on the pulse power. The 90° pulse duration at a particular power is thus a Q characteristic of the probehead.

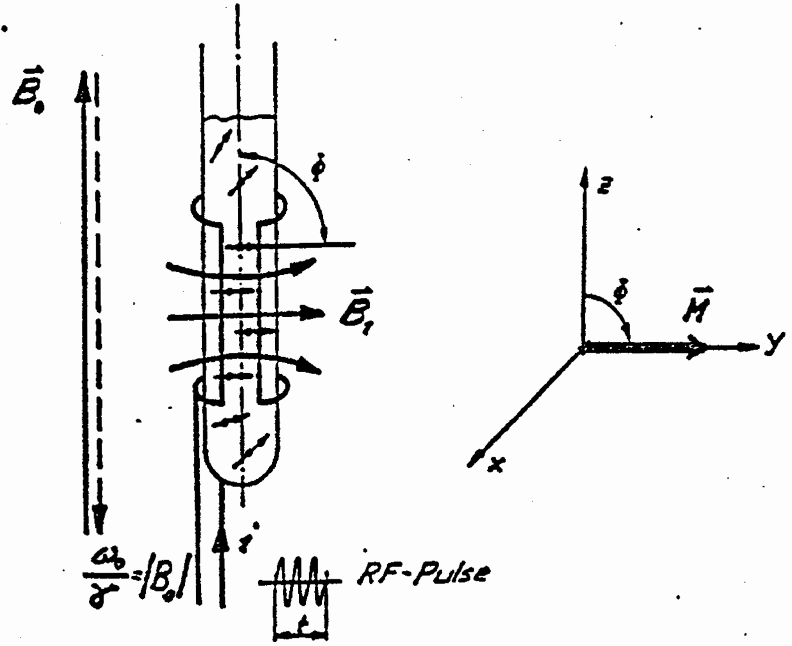

Figure 3.2: Transmitting Phase

When the magnetic field $\vec{B}_1$ is switched off, the nuclear spins precess in the static magnetic field $\vec{B}_1$ and relax back into their equilibrium state, i.e. the magnetization ($\vec{M}$) tilts back to its original alignment along $\vec{B}_0$. This motion induces a small voltage in the coil (figure 1.3).

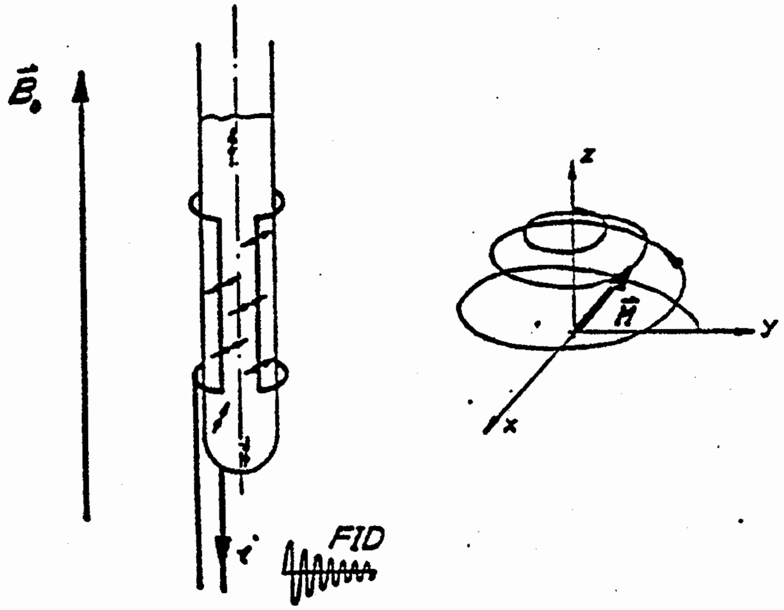

Figure 3.3: Receiving Phase

A transmitting circuit is needed to generate the RF pulse which creates the $\vec{B}_1$ field in the coil (figure 1.4). Here C_1 is used to adjust the resonance frequency (tuning) and C_2 is used for matching to 50 Ω (matching). Only one coil is used for transmitting and receiving, therefore a fast Transmit/Receive (T/R) switch must be present to switch between the two modes. (The operation of the T/R switch is explained in Part b2, RF technology).

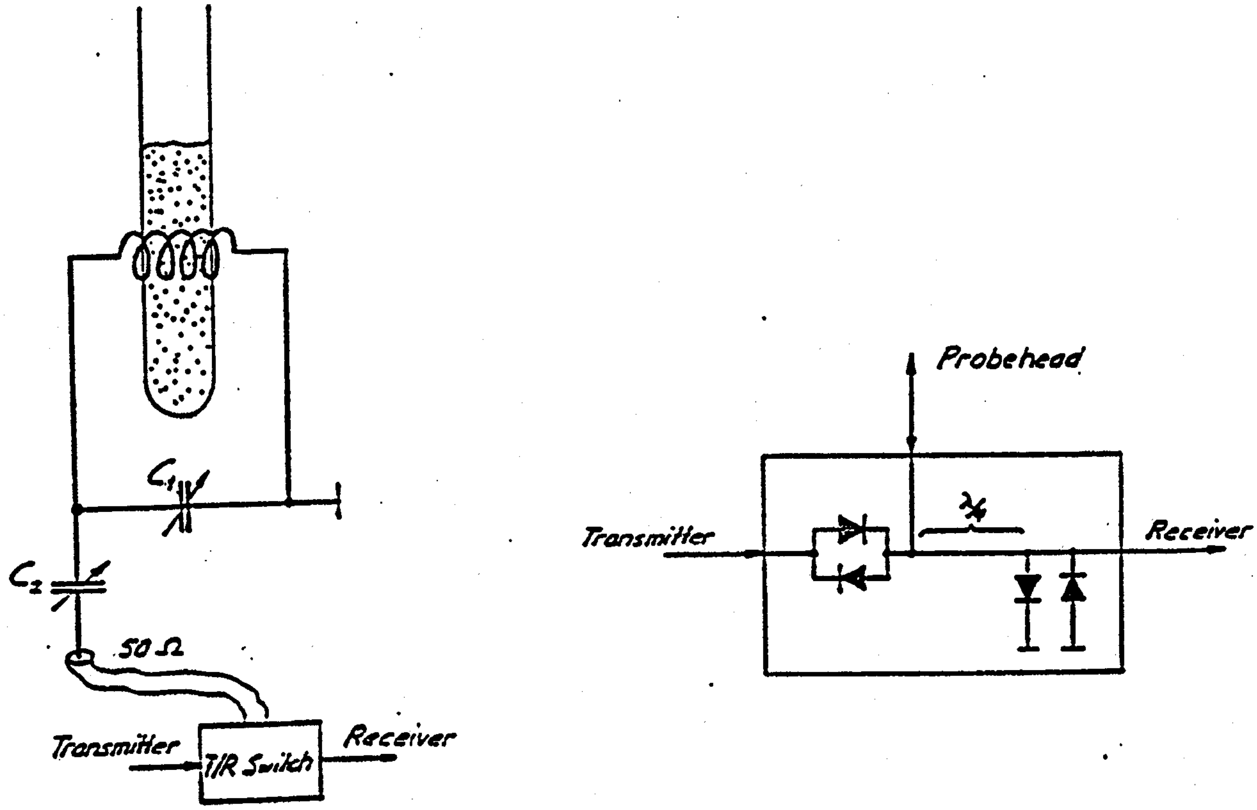

Figure 3.4: a) Oscillating circuit

b) T/R Switch

To stabilize the magnetic field (lock) and to decouple certain atoms, Further transmit and receive channels are usually necessary in high resolution NMR, for the lock signal (magnetic field stabilization) and to saturate a specific kind of nuclei for decoupling purposes. The standard configuration (shown in figure 1.5) has the observe nuclei on the inside coil and the outside coil doubly tuned for decoupling as well as for lock.

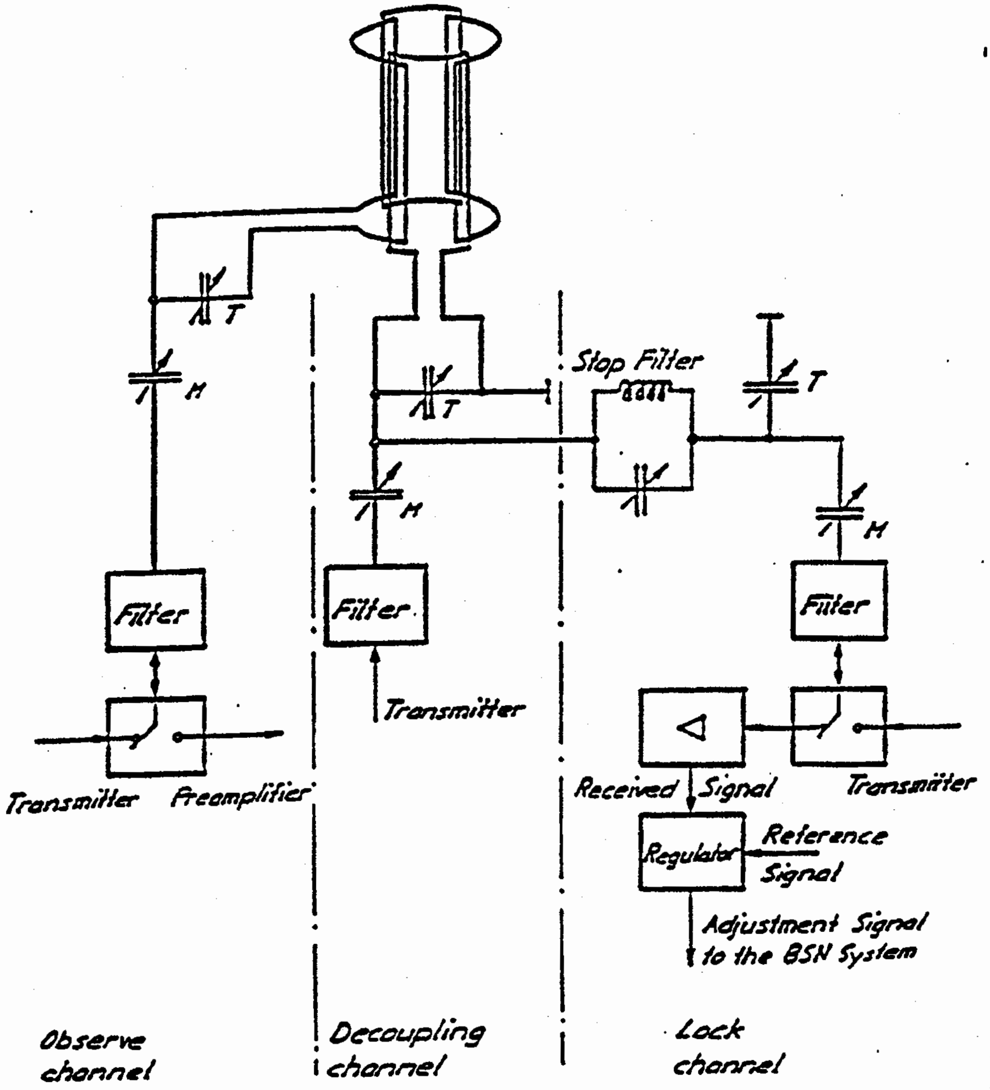

Figure 3.5: Basic Circuit

3.2 Sensitivity, pulse widths, H1 homogeneity, dead time

3.2.1 Probe sensitivity

is a function of several main factors:

1. Quality factor of the coil, Q
2. Filling factor of the coil, F
3. Efficiency of the circuit design
4. Circuit temperature

The quality factor Q of the circuit is mainly determined by the resistance of the coil wire and the quality of the capacitors, to some extent also dielectric damping of the probe glass and ceramic parts contribute to the over all quality factor.

The filling factor is given by the coil insert glass inner diameter which must leave some space for temperature control gas to pass through along the sample tube. For measurements using the outer coil (^{1}H observation on dual probes) however, the filling factor cuts down sensitivity.

The circuit efficiency is somewhat ill defined. The coil geometry is one of the subfactors. The optimum geometry of a Helmholtz coil (or saddle coil) has been calculated (Golay configuration) to have an angle of 120° and a 1:1.7 relation between width and height. This cannot always be fulfilled because of homogeneity constraints and in practice the best geometry must be found by trial and error.

The circuit temperature determines the thermal noise generated by the circuit and therefore has an influence on the signal-to-noise (S/N) ratio. The noise voltage is approximately proportional to the square root of the temperature (T). However, the probe is not the main source of noise so the influence on S/N is not very important. However, the Q factor also changes with temperature and this may have a noticeable effect.

3.2.2 Pulse length

Depends roughly on the same factors as probe sensitivity. For a given design, the pulse power which is available from the transmitter will determine the pulse length. Also, the gyromagnetic ratio (γ) of the nucleus to be observed is important:

$$\mathrm{Pw}_{(pulselength)} = f\left(\frac{Q \times \sqrt{(pulsepower)}}{\gamma}\right) \tag{3.1}$$

$$\tag{3.2}$$

In general, shorter pulses are achieved with small volume probes of high Q for high frequency nuclei with high transmitter power. The following table gives a rough overview over pulse lengths one can expect with high resolution probes. This table is valid for the low power amplifiers, which put out 250 - 300 watts for the X-nucleus range and 50 watts for the ^{19}F/^{1}H range, with a standard 3db attenuator at the output. This halves the available pulse power and makes the the pulses longer by $\sqrt{2}$. Usually, lower field instruments have somewhat shorter pulses because of more efficient probe circuits.

Probe	Nucleus	Diameter	PW (μsec)
^{1}H fixed	^{1}H	5	5-7
	^{1}H	10	7-12
^{13}C fixed	^{13}C	5	6-10
	^{13}C	10	8-12
	^{13}C	20	20-30
^{15}N fixed	^{15}N	10	12-15
	^{15}N	20	30-35
BB	^{15}N	10	14-17
	^{15}N	20	35-45
	^{13}C	10	12-15
	^{13}C	20	25-35
	^{31}P	10	12-15
	^{31}P	20	25-35
Decoupling coils, with DP = 6H - 8H			
	^{1}H	5	7-15
		10	12-20
		20	25-35

The 3 db attenuation is recommended to ensure that the probe can take the pulse power under any conditions. The pulse lengths as listed above are sufficient for all measurements. Experiments which are critical for 180° pulses should not be carried out with 20mm probes if possible, since there the π pulses might not be adequate for optimum results; also the H1 homogeneity will present a problem.

3.2.3 H1 homogeneity

Similarly to a sample in a H0 magnetic field which does not experience the same field at any position because of field inhomogeneities, a sample in an irradiation field H1 does not experience the same H1 field at every position. Tightly wound solenoid coils provide the best H1 homogeneity, but for ease of use all high resolution probes have Helmholtz (saddle) coil arrangements. There the H1 homogeneity is always quite bad, especially since the sample must always be larger than the coil to provide good resolution. The H1 homogeneity can be measured as the residual signal after a π pulse compared to the $\pi/2$ signal intensity. In Helmholtz coil designs, 5 - 15% residual signal must be expected. For multiple pulse experiments, bad effects due to H1 inhomogeneity can be suppressed by phase cycling. For some solids experiments, H1 inhomogeneities of less than 1% are necessary. Such experiments can only be carried out in solenoid coils which are optimized for good H1 homogeneity.

3.2.4 Dead time

The dead time is the recovery time of the probe circuit after the pulse. Any resonance circuit which is excited at its resonance frequency will oscillate at this frequency for some time. In order to see the much weaker NMR signal after the pulse, this oscillation must be dampened below the level of the NMR signal. Simultaneously, the receiving system of the spectrometer also needs some recovery time after the pulse which is called the instrument dead time. In addition, there is the so-called "acoustic ringing" dead time of the probe which can be quite severe at low frequencies.

3.2.5 Instrument dead time

The MSL receiving system is optimized for short dead time since this is essential for solids wideline spectroscopy. Preamplifier dead time and receiver dead time are as short as 2 - 3 μsec. However, there is one component in the receiving "chain" which may have a longer ring down time, that is the butterworth audio filters which generate most of the baseline distortion due to dead time acquisition. Therefore, the dead time delay must be optimized for the filter width used, when a flat baseline is required. Usually, the filter width should be set to twice the normal value in these cases.

3.2.6 "True" probe dead time

The true probe dead time is determined with the probe outside the magnet as the time after the pulse when the noise "looks normal"[1]. This test is preferrably done with a large sweep width and fully open filters (FW = 2E6). The dead time is then digitized and can be measured as number of "bad" data points * DW. The true probe dead time is a function of the circuit quality (Q), since in a high Q circuit an oscillation is less quickly damped away by losses of energy.

3.2.7 Acoustic ringing dead time

Acoustic ringing is measured as above, but with the empty probe inside the magnet. This phenomenon is somewhat ill defined, but it can be visualized as mechanical vibration of probe material which is excited by the high power pulse. This vibration then results in a voltage induced into the RF coil which decays just like an NMR signal. This signal may persist as long as a few milliseconds and may render observation of short FIDs impossible. Especially if samples or probe materials have piezoelectric properties, this ringing may be quite severe. High quality sample tubes or quartz glass show piezoelectric ringing and should not be used if ringing is a problem. Other solutions for acoustic ringing involve appropriate mechanical damping of probe parts and sample which shift the ringing frequency out of the spectral range of interest.

3.2.8 RF interference, filter requirements

An NMR probe is basically a RF antenna, so a probe will always pick up frequencies which are "on the air". These pickup frequencies may be much larger than the observed NMR signal and must therefore be removed. Inside the probe two major pickup frequencies are introduced by the spectrometer itself, decoupling frequencies and the lock frequency. The probe itself contains some filtering devices which reduce the interference between lock/decoupling and the signal channel. These devices are stop filter circuits and the mechanical arrangement of the coils. Usually, decoupling and lock are tuned on the outside coil which is orthogonally located compared to the observe coil which already damps the interference just like a badly oriented antenna. Nevertheless additional filtering is required. The preamplifiers and the preamp-matching boxes contain additional deuterium and proton filters. In addition, the

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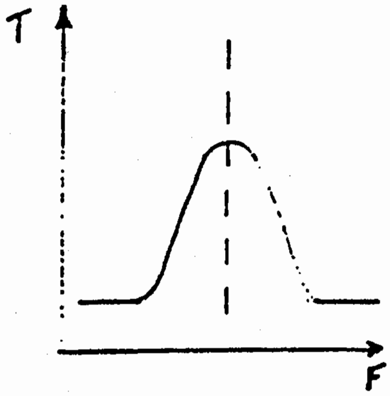
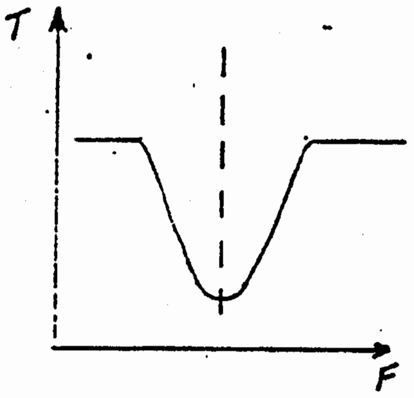
[1] However, this ignores magnetoacoustic ringing

lock and decoupling frequencies must be fed through bandpass filters to prevent any "impurities" of lock and decoupling frequencies from getting to the preamplifier amplification stages. These bandpass filters are usually best located between the lock/decoupling transmitter outputs and the probe. If decoupling is applied at any other frequency but protons, an additional reject filter for this decoupling frequency in the signal path between probe and preamp is necessary. For ^{19}F lock, a ^{19}F bandpass must be used in the lock channel. For CW decoupling at very high power or for long high power pulses, bandpass filters are not suitable since they actually convert some power into heat and may burn out. High pass or low pass filters must be used then.

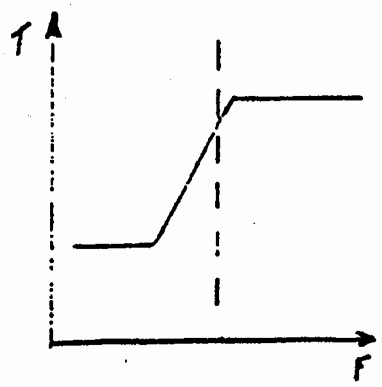
a) Filter characteristics:



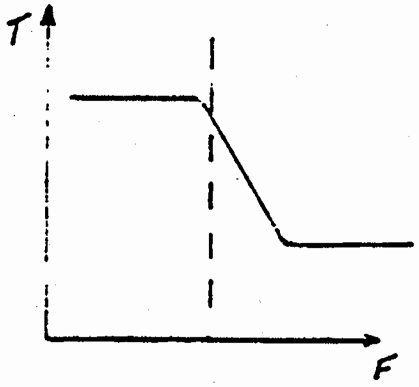
Band Pass



Band Stop



High Pass



Low Pass

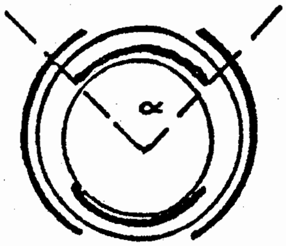
Sometimes, stray frequencies from outside may be picked up by the detection circuit, for instance from FM radio stations or other RF sources. Then you should call your Bruker service engineer since these problems may be complicated.

3.3 Coil sizes and sample volumes

The coil size for different sample diameters is a compromise between shimmable volume and coil geometry. Best sensitivity per volume is achieved with smaller sample diameter.

Sample diameter	Coil height (Z) Observe	Decouple	sensitivity (normalized)	min. sample volume
5	14	18	1	0.5
10	23	27	3	2
15	30	36	4.5	5
20	37	38	6	11

The coil arrangement of two concentric coils is always orthogonal to minimize crosstalk between coils. For optimum sensitivity, the angle α of the coil and the height of the coil must be optimized, the height of the coil is limited by shimability.



3.4 The Probehead in the Spectrometer

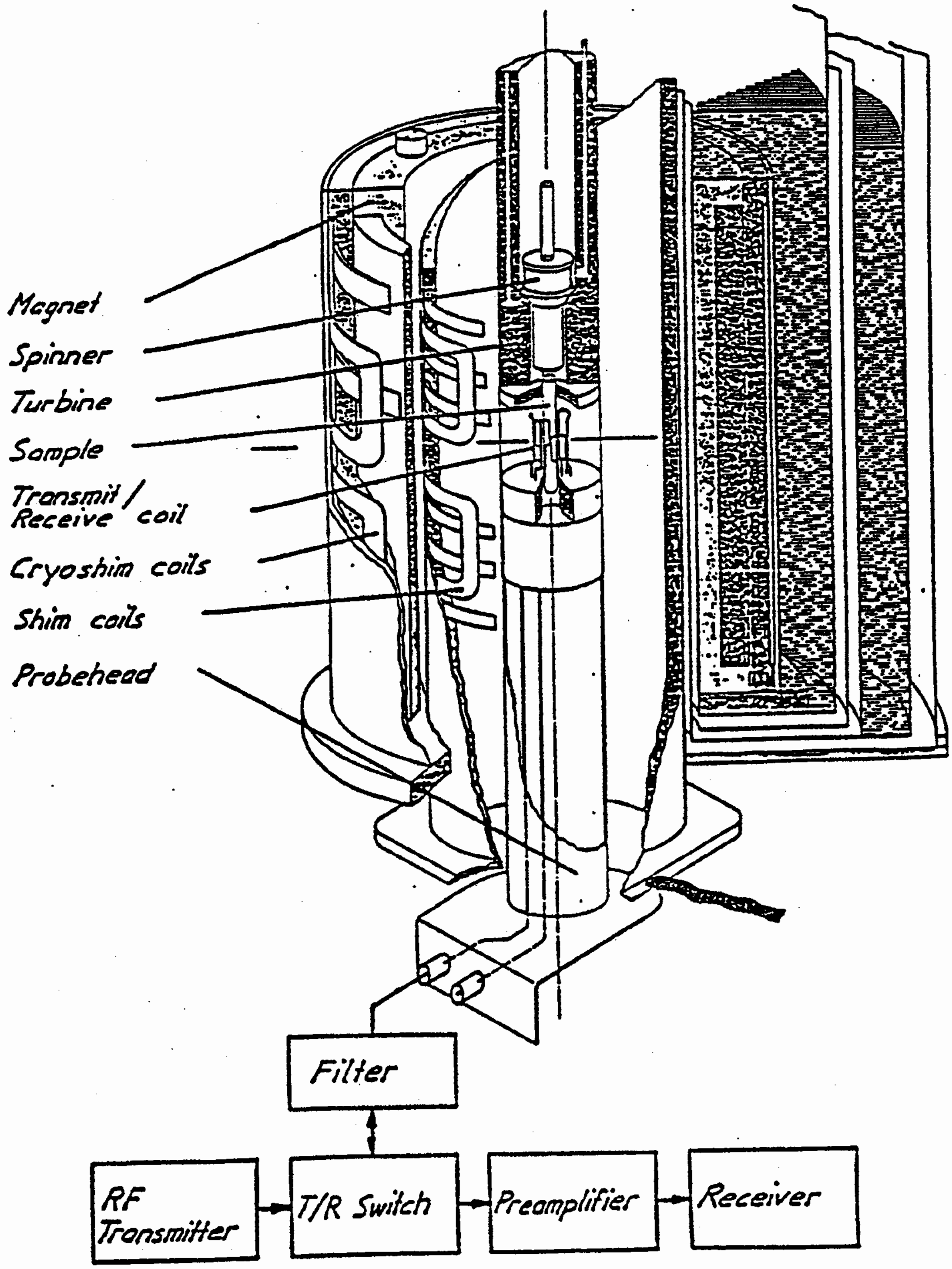
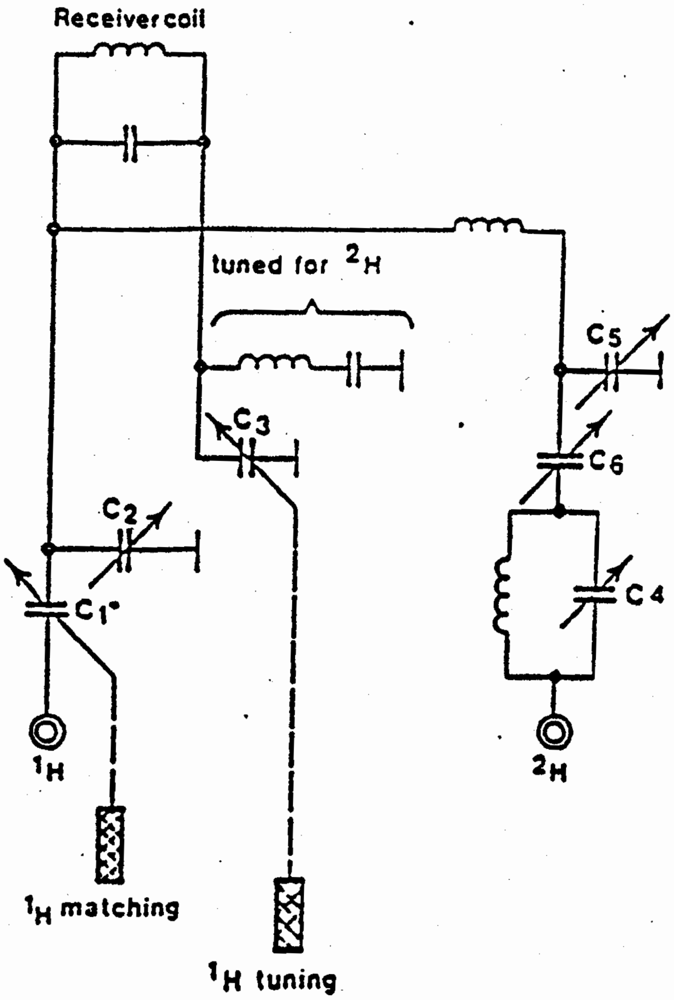


Figure 3.6: Basic layout

3.5 Circuit diagrams

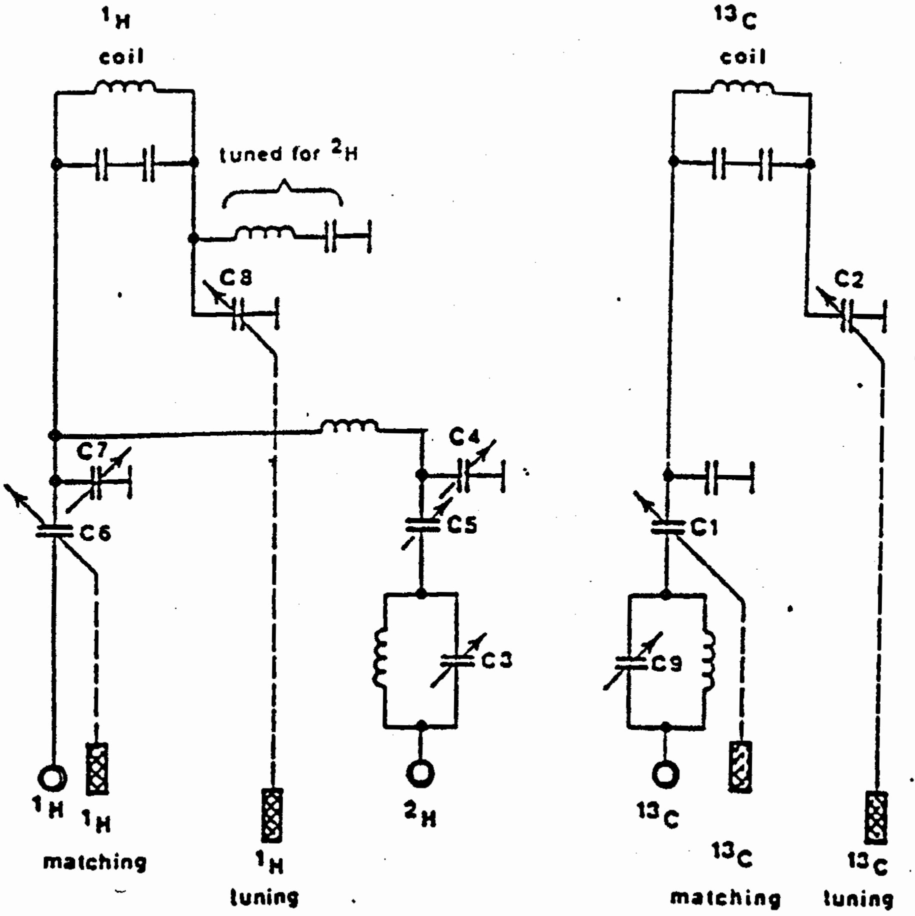
The circuit diagrams are very similar for all probes so only three diagrams are given to show the principles.



Tuned for resonance :
C_2, C_3, C_5
Tuned for matching :
C_1, C_6
Tuned to stop ^{1}H into ^{2}H:
C_4

Figure 3.7: Fixed frequency proton probe with ^{2}H lock.

Sensitivity is optimized for one frequency. In this case, lock sensitivity is sacrificed for proton sensitivity. Any kind of double tuning will however cost some sensitivity for both frequencies; this becomes more severe if the frequencies are close together. Since ^{1}H and ^{2}H frequencies differ by a factor of 7, double tuning only costs 10 - 15 % for ^{1}H. This is about the same as having two separate coils (one for ^{1}H the other for ^{2}H) would lose. If ^{13}C and ^{31}P double tuning is required, losses of 40 - 60 % are inevitable.



Tuned for symmetry:
(no ^{1}H at)
C7, C8
Tuned to stop ^{1}H into ^{13}C.
C9

Tuned for resonance:
C2, C4, C7, C8
Tuned for matching :
C1, C5, C6
Tuned to stop ^{1}H into ^{2}H:
C3

Figure 3.8: ^{13}C/^{1}H dual probe

Since here the proton coil is the outer coil, sensitivity is about half of the proton fixed probe. When such a probe is shimmed, not only the disturbing influences of the outer coil (which are smaller in this case since the coil is further away from the sample) but also the influences from the inner coil must be shimmed out.

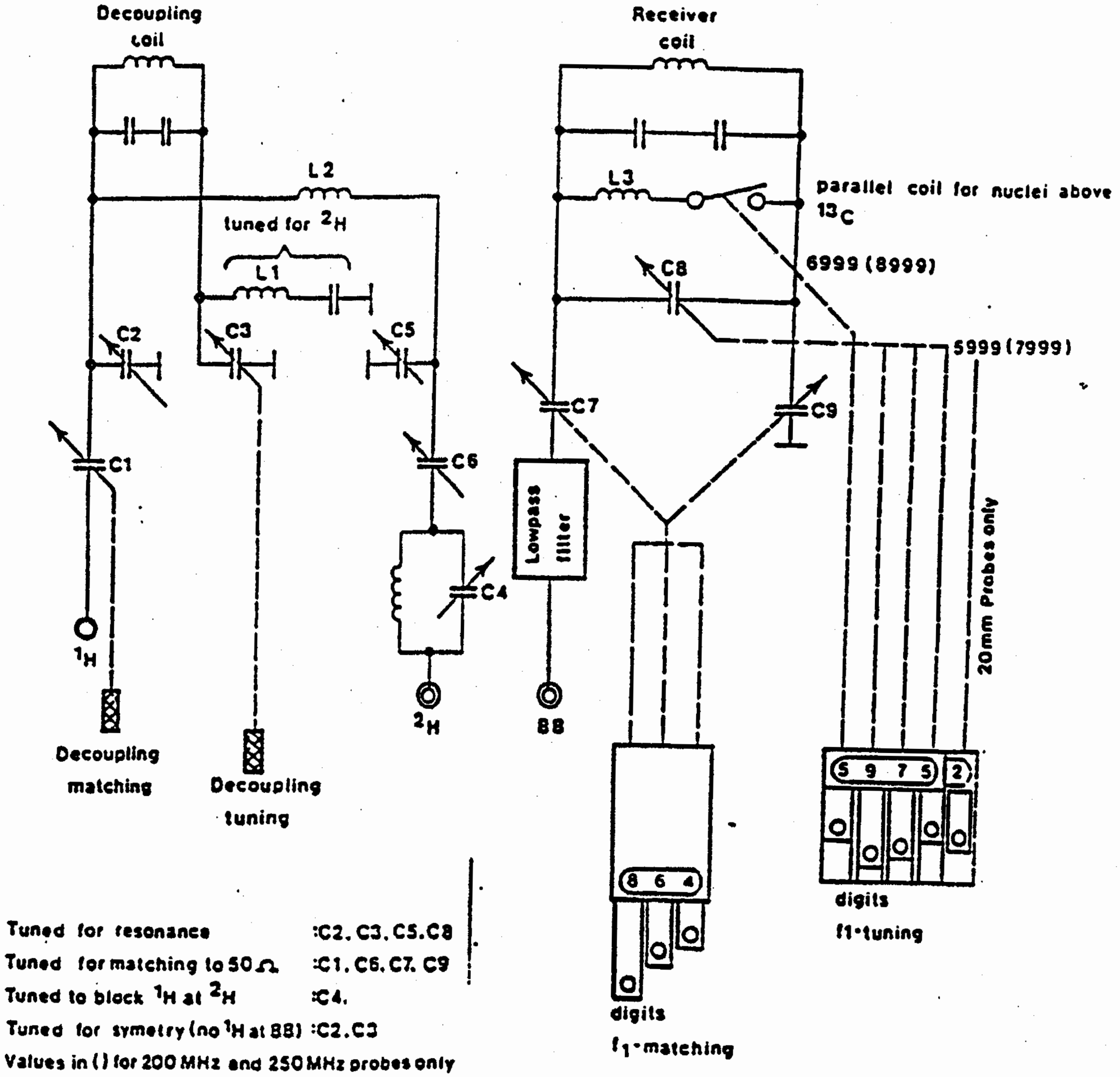


Figure 3.9: Multinuclear (BB) probe with proton decoupling

The decoupling circuit is the same as for the previous probe. The X-circuit has a "digital" switch for both tuning and matching to provide a large range of capacitance. The tuning switch has two additional functions: it changes the capacitance of the parallel capacitor and it switches a parallel coil for high frequencies (^{31}P). This parallel coil reduces the sensitivity for high frequencies but it is necessary to reach these high frequencies with a given coil inductance. This coil inductance is optimized for ^{13}C. The matching switch changes two capacitances simultaneously to preserve symmetric tuning for the X-circuit. The multinuclear design loses about 20 % in sensitivity versus a fixed frequency probe for ^{13}C. For nuclei with resonance frequencies below ^{109}Ag, a low range probe is available.

3.6 Inserting the sample into the probehead

Figure 3.2 shows the sample and spinner located inside the shim system and probehead. The sample tube is first fitted into a spinner, the depth of the sample tube is critical so that the sample is aligned within the center of the coils. Upon placing the spinner and sample tube into the magnet (turbine housing) the spinner is then brought to the desired speed by adjusting the amount of drive air to the turbine housing. The spinning speed is monitored by a infrared sensor. Poor quality sample tubes (exhibiting variations in wall thickness, straightness and concentricity as well as glass impurities) can lead to poor resolution and will have a considerable effect on the spinning side bands (SSB) in the spectrum.

The spinners can also give these same results as a poor quality sample tube. For this reason, the manufacturing tolerances lie at ±1μm. Depending on the temperature of the sample being measured, the spinners are made of teflon (ambient) or of ceramic (high or low temp.).

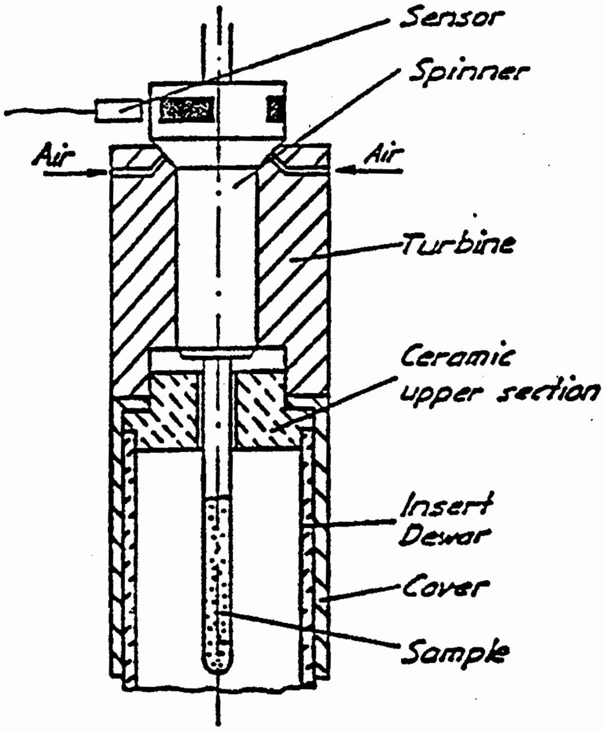


Figure 3.10: Spinner and Turbine housing

3.7 Sample Rotation

If the magnetic field $\vec{B}_0$ in the XY plane is not homogeneous the spins at different locations within the sample tube see different field strengths, thusly they will resonate at slightly different frequencies. The results will be broadening of the lines and resolution becomes poor. If one now allows the sample tube to rotate about its own axis, an atom "migrates" from position C to D and again back to C, etc. (figure 3.1). If the rotational speed is sufficient (20 to 50 Hz), the nuclei can no longer follow the field variations and consequently sees an average field strength.

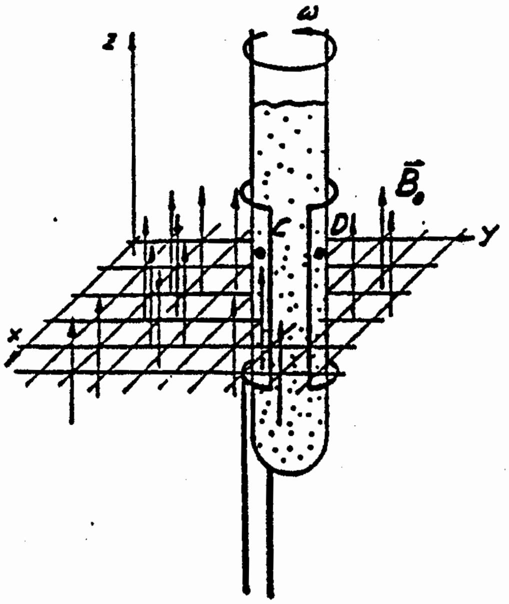


Figure 3.11: Inhomogeneous Field Distribution in the XY Plane

The frequency of the response signal likewise corresponds to this average field strength. The improvement of resolution through spinning works only in the XY plane. Z-shims (up to the 5th order) must be used for homogenization in the Z-direction.

3.8 Probe background

Bruker probes are optimized for minimal background signals, but they must be made out of something, which may give an NMR signal for other nucleus. For high resolution measurements probe background is never such a problem as in wideline NMR since the background signal is always much broader than the desired signal. Only for proton, flourine, boron and silicon there may be a really disturbing background problem. For protons, the background signal is mostly absorbed humidity, for flourine it is the ^{19}F contained in coaxial cable and ceramic parts, and for boron and silicon it is the glassware. There are special probes available for background-free observation of ^{19}F and ^{29}Si, the proton probes just must be dried before use. The ^{1}H/^{19}F dual probe has a small background on both frequencies.

Special importance is to be given to the choice of materials, since these can have major effects on the spectrum. When the nucleus being measured is present as a structural material or as a contamination, an undesirable background signal will result.

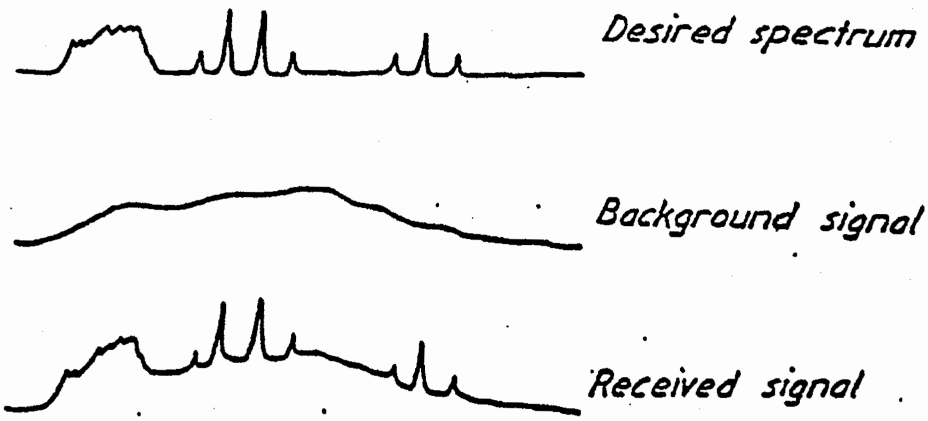


Figure 3.12: Background Signal

Nuclei, for which a background signal can be present are:

^{1}H	-from moisture
^{19}F	-from ceramic parts and teflon coaxial cable
$^{29}Si + {}^{11}B$	-from ceramic parts and glass
^{27}Al	-from ceramic parts and capacitors, from Al metals
^{63}Cu	-from coil wire

3.9 Variable temperature operation

A NMR probe is not a furnace, nor is it a cryostat. The current probe design is a compromise between sensitivity, production costs, and temperature range. Therefore, extreme temperature ranges can only be achieved with special probes. Generally, small volume probes can go to more extreme temperatures than large volume probes.

To operate the probehead at it's specified temperature range, a temperature regulation system is necessary(BVT-100 or the Eurotherm). The temperature is sensed by a thermocouple or a PT100. The sample is maintained at temperature by means of cooled or heated air. The air is cooled with liquid nitrogen if necessary, and subsequently is brought to the desired temperature by means of a heating coil.

The structural materials of the probe have different expansion coefficients, which makes it difficult to adhere to mechanical tolerances.

With Bruker standard probes and temperature unit, the following ranges are achieved:

5mm:	-150° to +180° C
10mm:	-130° to +150° C
20mm:	-80° to +100° C

For extreme temperatures, special probes down to -170° C and up to +400° C with special insulation are available.

For variable temperature operation, the following safety hints should be observed:

- Make sure the thermocouple is properly positioned. The thermocouple tip should be at least 3 - 5 mm above the bottom ceramic piece. The lengths of thermocouples can differ quite a bit, so the adjustment must be done for each probe/thermocouple combination.
- Flush ambient air through the gap between shim system and magnet bore.
- Use a ceramic spinner.
- Pump temperature control gas out of the shim system eject line or at least remove eject line from the shim system.
- Change temperature gradually.
- Set heater power just high enough to reach the desired temperature.
- Make sure that temperature control gas is flowing and properly connected.

3.10 Coil surfaces

Skin effect:

The currents for RF flow only along the surface of the conductors. The penetration depth is 0.5 - 10 μm, depending on the frequency. A large diameter is therefore necessary for a low resistance. Because of this skin effect, great attention must be paid to the surface of the conductors.

The conductivity must be good and the surface must be as smooth as possible.

Proximity effect:

If several conductors with current flowing through them lie close together , less current flows in the neighborhood of the closest approach than in the conductors that are far apart, figure 3.11. This implies a greater resistance and a lower Q.

A larger structural design would therefore be better. However, since space is limited, compromises are necessary. The tight structure also causes eddy current losses in the shielding.

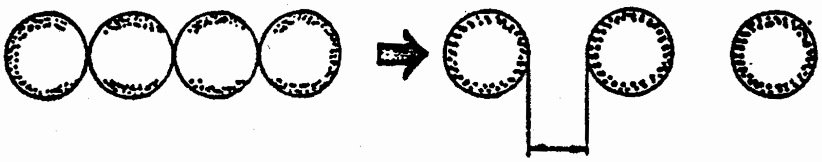


Figure 3.13: Proximity effect

Susceptibility:

There are non-ferrous metals with negative susceptibility and others with positive susceptibility .

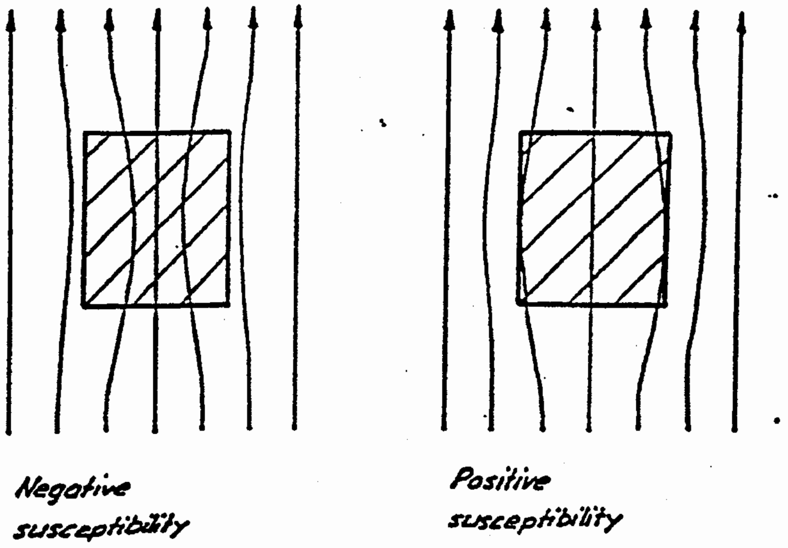


Figure 3.14: Susceptibility

Since copper with a negative susceptibility is used as the coil material, another material with a positive susceptibility must be added, figure 3.12. The amount is chosen so that the susceptibility towards the outside becomes zero. The magnetic field $\vec{B}_0$ is thus no longer affected. The field displacement would cause a larger base in the spectrum.

Feed lines to the Receiving Coil:

The feed lines to the receiving coil may not enclose an area, since otherwise signals would also be received there. This would cause a shoulder peak in the spectrum, figure 3.13.

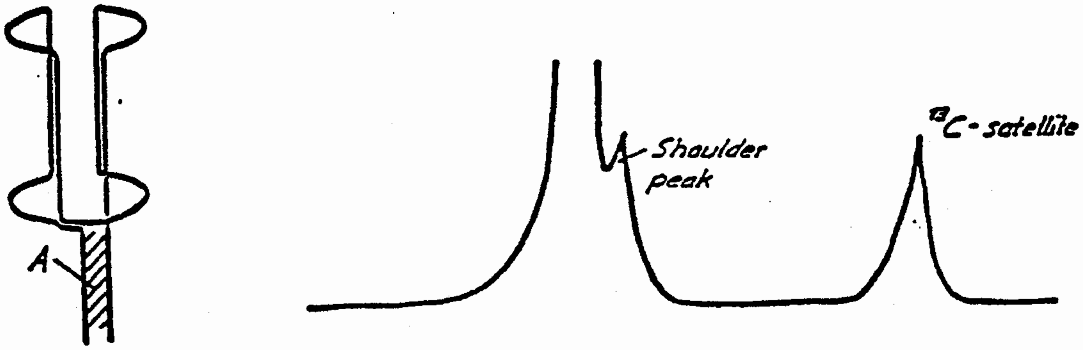


Figure 3.15: Influence of Feed Lines

3.11 Electronics

3.11.1 Matching

The standing wave ratio (VSWR, SWR):

Definition: $VSWR = \left(1+\sqrt{(P_{refl}/P_{fwd})}\right) / \left(1-\sqrt{(P_{refl}/P_{fwd})}\right)$

P_{refl} is the reflected power coming from the probehead.
P_{fwd} is the forward power going to the probehead.

Range of values: $1 \leq \text{VSWR} \leq \infty$

- Example

If a matched attenuator is inserted into a matched system, the power in the load becomes smaller by the damping of the attenuator (figure 3.6).

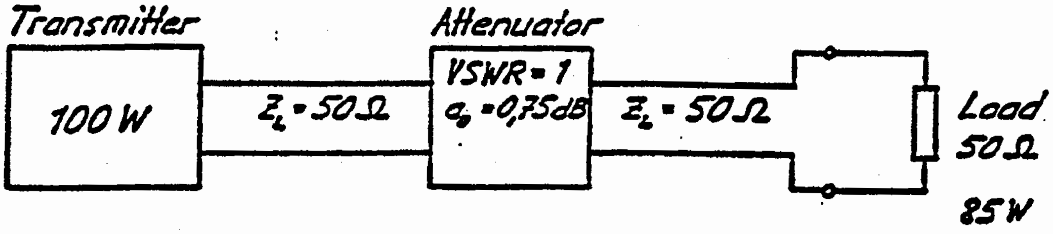


Figure 3.16: Matching

When inserting anything (i.e., the reflection display or reflection bridge) not matched for 50 Ω transmission line, then tuning the probehead will not match it to 50 Ω.

If the tuning is done at the spectrometer (figure 3.7) , the T/R switch and one or more filters are situated between the reflection bridge/display and the probehead. If the T/R switch and the filter have a VSWR > 1, a reflection of power will occur. As a consequence, the matching capacitors in the probehead are adjusted so that no standing waves will occur between the reflection bridge/display and the matching box. If the tuning range is not sufficient or the 50 Ω match no longer exists at the probehead, standing waves can occur between the T/R switch and the probehead, increasing losses. Also the transmission line length between the preamp housing and the probehead has a considerable effect.

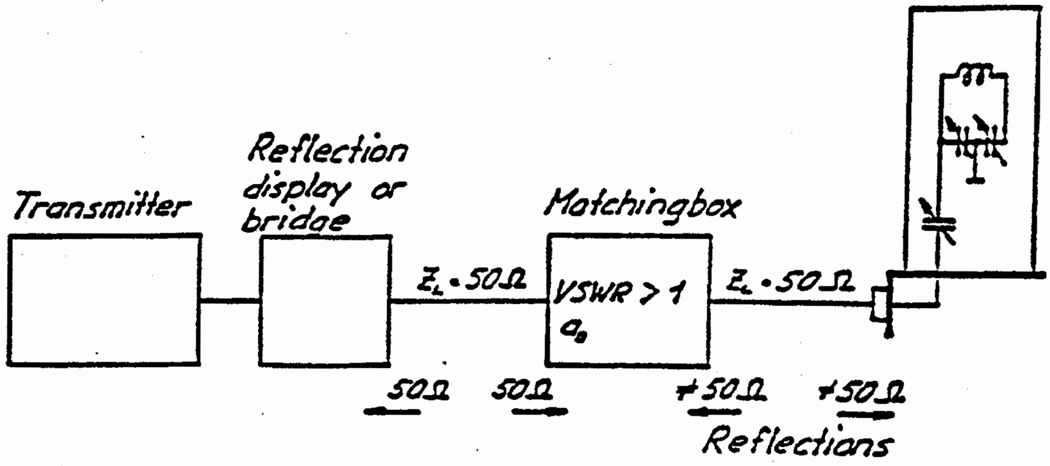


Figure 3.17: Matching at the spectrometer

3.11.2 Testing the Probehead

- **Testing the Symmetry:**
  A wire loop (pickup coil) is inserted in place of the sample within the coils. A voltage of 500mV is applied to this coil. The induced voltage into the probe coils then depends on the quality factor (Q), coil geometry, and the symmetry of the circuit tuning.

- **Power Test:**
  To test the probehead for arcing at the customers site, the measurement setup shown in figure 3.10 is used. The oscilloscope must be connected to a channel other than the transmitter (it does not matter if this is lock, decoupling, or a third channel). The frequency of this output does not matter, since the signal of the transmitter is always visible, due to crosstalk between the two coils.

  The transmitter is set to the desired power. Then the attenuator is switched step-by-step from a large attenuation to a smaller one. The amplitude of the signal must increase at each step (to be observed on the scope). As soon as the amplitude no longer increases or even becomes smaller, the maximum power has been reached, i.e. the probe is breaking down (arcing).

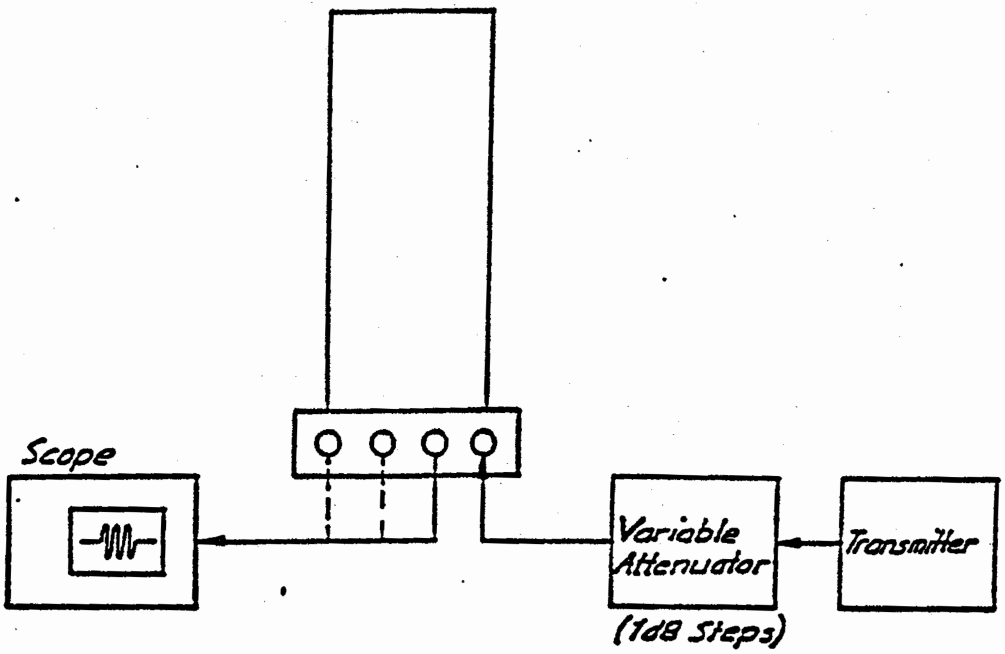


Figure 3.18: Power Test

Chapter 4

High power probes

4.1 Design principles

High power probes are optimized for the following properties:

- Short pulses, high power handling capabilities
- Short dead time, low Q, high bandwidth (except CP probes)
- Good RF homogeneity

4.1.1 Low Q

The Quality factor (Q) of the resonance circuit is given as $\omega * L/R$, where ω is the frequency. This does not tell a whole lot, but in principle it says that the coil must have high inductance (L) and low resistance (R) to achieve high Q. The capacitance must have high resistance at the resonance frequency. Usually, the Q is too high for wideline probes so it is artificially spoiled by low inductance resistors of about 2 Ω total.

4.1.2 Power handling capabilities

The maximum power which a probe can handle is given by the maximum RF voltage appearing at some point of the circuit and the breakthrough voltage of the components used in the circuit. The maximum voltage is approximately

$U_{(max)} = (U_{(input)} * Q)/50$

for 1 kw power $U_{(input)}$ is about 600Vpp, so $U_{(max)}$ is about 600 for Q = 50, about 3 kv for Q = 250. For all high power probes, tuning capacitors of 5 kv up to 15 kv rating are used, all support material used is highly insulating dielectric, and sharp edges are avoided especially at "hot spots". However one has to bear in mind that warmup effects especially during long pulses may deteriorate performance, and that dirt or even a humid atmosphere may grossly change breakthrough voltages.

4.1.3 Dead time

The electronic dead time is approximately given by:

$\tau = 10 * 2Q/\omega$

so for 100 MHz, Q =100, $\omega = 100 * 2\pi$, $\tau = 3.2\mu$sec

for 10 MHz, Q = 500, $\tau = 60\mu$sec

4.1.4 Bandwidth

The bandwidth $\Delta\nu$ of a probe is given as $\Delta\nu = \nu/2Q$, so for a Q of 100 and a resonance frequency of 100MHz, the bandwidth between 3 db points is 0.5 MHz.

4.1.5 H0 homogeneity

Good homogeneity is not important for high power probes (except CP-MAS probes). The resolution which can be achieved lies between 1 - 50 Hz depending on geometry and nucleus. This resolution difference comes mainly from three factors:

- The solenoid coil geometry cannot easily be shimmed in a shim system optimized for saddle coil probes.
- The coil wire is not susceptibility compensated.
- Sample spinning is not used (except MAS probes).

Therefore, those probes are used for:

- Broadband measurements on solids.
- Measurements of broad lines in liquids, for instance solutions of quadrupolar nuclei or paramagnetic molecules.
- NQR measurements

For line narrowing experiments in solids, good RF performance is a prerequisite for efficient line narrowing, and the linewidths achieved are still orders of magnitude larger than in high resolution in liquids, so the high power probe design principles must be used.

4.2 Summary

The high power probe family consists of the following probe types:

- ^{1}H or ^{19}F wideline probes, 5mm solenoid coil. This probe can also be used for multiple pulse line narrowing (homonuclear dipolar decoupling). The Q factor of these probes is about 100, the electronic dead time is 2.5 - 4 μsec.
- X-nuclei "broadband" wideline probe, inserts with 10mm solenoid coils standard, 5mm or larger diameters optional. Those probes are for X-nuclei wideline observation without decoupling. For experiments where RF performance is less critical and ease of handling is preferred, these probes can also have saddle coil inserts (10mm standard, larger diameters optional). The standard frequency range covers ^{109}Ag to ^{31}P. For lower frequencies or $^{203,205}Tl$, special inserts are available on request. Observation of $^{203,205}Tl$ requires special equipment!

  The Q factor of these probes is in the order of 50 - 70, the electronic dead time is 3 - 30 μsec .
- Cross-Polarization (CP) probes are available with or without magic angle sample spinning (MAS). These probes are not optimized for short dead time in order to get the best possible sensitivity and high RF fields with moderate power requirements.

The solenoid coil is double tuned to two resonance circuits, one for observation and one for decoupling. The circuitry is designed to get good RF efficiency for the decoupling channel and good sensitivivty for the observation channel. The decoupling channel may be factory tuned for ^{1}H or ^{19}F, the observation circuit is tunable over a fairly wide range to cover ^{15}N up to ^{31}P with two separate probes. The X-tuning range can be shifted within certain limits to fit the customers requirements. The Q factor of the X-channel is about 100 - 150, of the decoupling channel 200 - 300, the electronic dead times are 20 - 50 μsec and 4 - 6 μsec. Sample sizes are 7.5mm and 5mm for CP probes and 7 or 4mm for MAS probes. Spinning speeds of 5KHz for the 7mm and 15KHz for the 4mm may be obtained.

These probes are used for narrower lines in solids where decoupling is necessary to achieve pure quadrupolar or CSA lineshapes (CP probes) and for line narrowing with spinning and decoupling. Since both frequencies are tuned on the same coil, cross polarization is effectively applicable if desired.

4.3 Special probes

4.3.1 CRAMPS probes

The CRAMPS probes are MAS probes which are tuned for either proton or flourine frequency. They are used for multipulse homonuclear dipolar decoupling experiments combined with magic angle spinning. They are optimized for good sensitivity, short dead time and high RF efficiency. Therefore these probes perform the CRAMPS experiment better than the decoupling channel of an ordinary CP-MAS probe.

4.3.2 Diffusion probes

The diffusion probe has basically the design of a X-wideline or ^{1}H/^{19}F wideline probe except for three major differences:

- The standard coil is a saddle coil of 7.5mm (optional 10mm) for ^{1}H/^{19}F and 10mm for X-nuclei.
- No damping resistors are used to keep the Q fairly high.
- The probe contains two gradient coils to generate a Z-gradient along the sample axis.

4.3.3 Cryo probes

The cryo probe is designed to work at temperatures down to 4° K inside a liquid helium cryostat. The sample can be exchanged through the probe body while the probe stays at low temperature.

4.4 Temperature ranges

The operating temperature ranges are:

^{1}H/^{19}F wideline probe	old: -150 - +150° C
	new: -170 - +300° C
X-nuclei wideline probe	-150 - +150° C

CP probes (stationary)	old: -150 - +150° C
	new: -170 - +300° C
CP MAS, CRAMPS probes	-120 - +150° C
Diffusion probes	-100 - +100° C
Cryo probe	-269 - + 30° C

4.5 The MAS Probehead: (Magic Angle Spinning)

With this probe, the sample rotates about an axis situated at an angle of 54°44′ to the Z-axis. At this angle, the Z-components of the local magnetic fields that are caused by the spin of the elementary particles, due to the Dipole-Dipole couplings of the nuclear spins (observable in solids), are equal to zero. Consequently the principal magnetic field $\vec{B}_0$ is no longer affected by the neighboring atoms. The sample rotation causes the average angle θ_{xy} between the Z-axis and the bonding vectors to become equal to 54°44′ (figure 3.3). (Ref. Part h1 for further information on MAS).

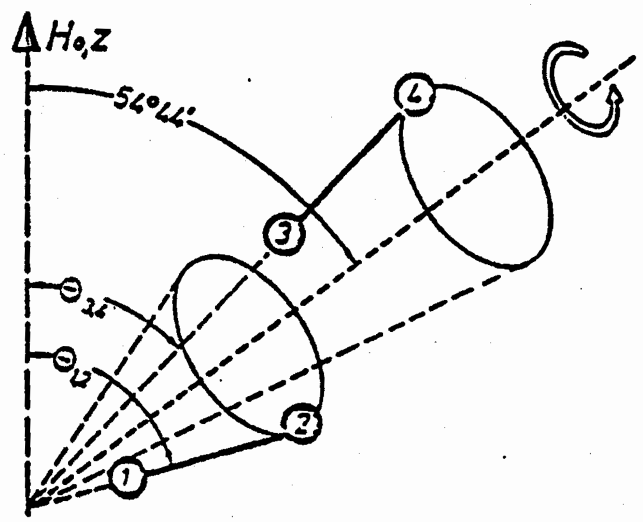


Figure 4.1: Magic Angle Spinning

In this figure $\langle\theta_{1,2}\rangle = \langle\theta_{3,4}\rangle = 54°44'$ but $\theta_{1,2} \neq \theta_{3,4}$.

The rotor with a diameter of 7mm and will spin up to 7 kHz. The pressure of the drive air is $\approx$ 2 bar. The rotational speed is monitored here as well with an infrared sensor. With

the high speed MAS probehead, the rotor diameter is 4 mm. Thus the spinning speed can be increased to 17 kHz.

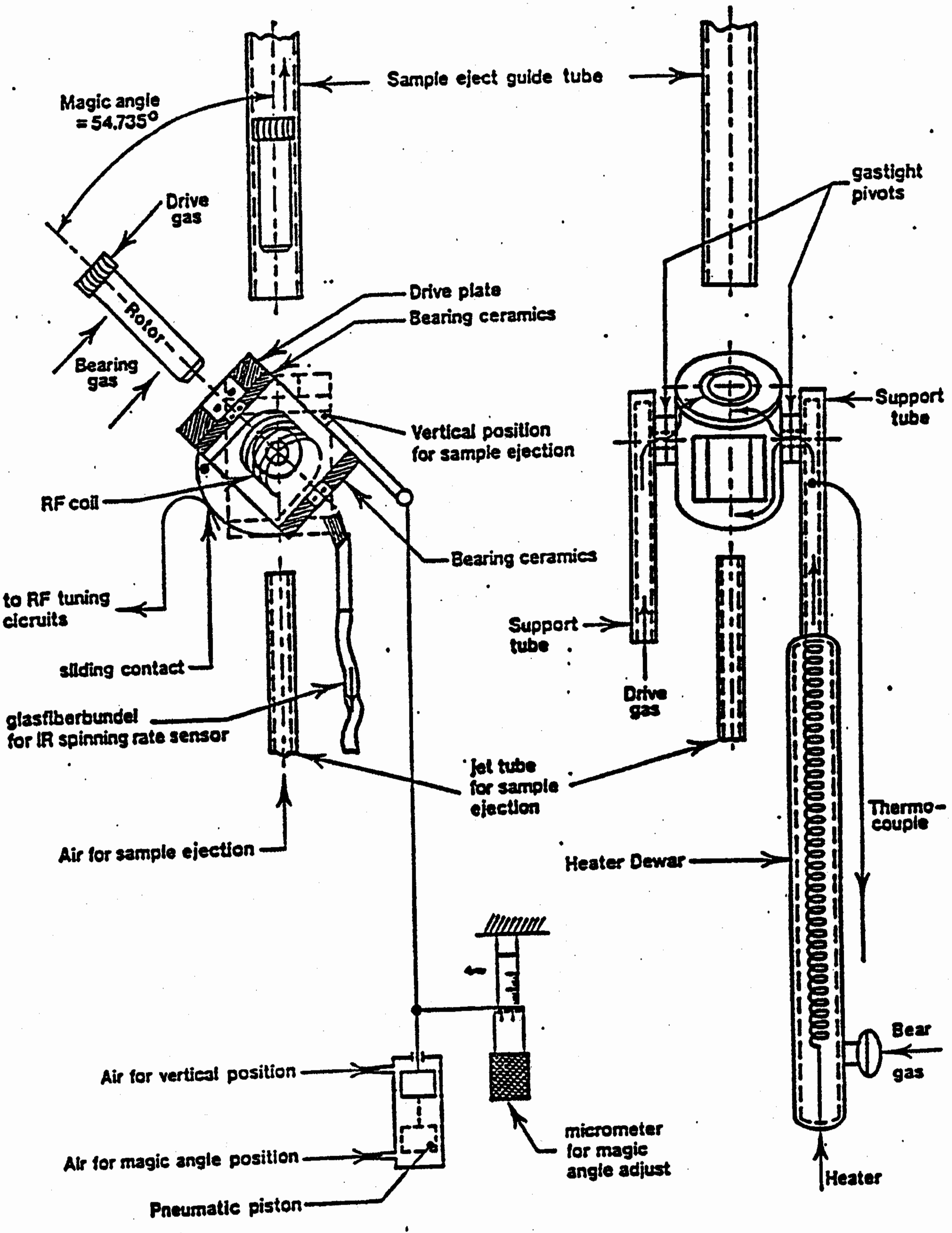


Figure 4.2: MAS-DAB Probehead

Chapter 5

Imaging probes

For vertical bore magnets there are two types of imaging probes available:

- micro-imaging probes
- mini-imaging probes

5.1 Micro-imaging probes

These probes are available for narrow bore and wide bore magnets. They contain a tuning circuit very similar to high resolution probes with exchangeable inserts for diameters 4 mm (solenoid), 5 mm, 10 mm, 15 mm, 20 mm, 25 mm (Helmholtz coils). Tuning ranges are for selected X-nuclei, ^{1}H or ^{19}F. Decoupling is also available for X-nuclei. The probe has built-in gradient coils for gradient strengths up to 70 gauss/cm. Air cooling is provided to remove gradient heat.

5.2 Mini-imaging probes

These probes are available for frequencies 200 MHz or higher. The coil is a cavity design optimized for high RF homogeneity. The sample size is 70 mm. The probes do not contain a gradient system. They must be used in super-widebore magnets with 150 mm bore diameter where the gradient coils are contained in the 150 mm shim system.

In imaging probes, dead time is not critical, but sensitivity is. So these probes are high Q designs (Q = 100 - 200).

High power probes As all probes, HP probes are fragile. Also, dirt and humidity may have disastrous effects on breakthrough behaviour. Service work which can be done by operators includes:

- Exchange of transfer dewars
- Probe cleaning with compressed air
- Coil and stator exchange in MAS probes

Service work which should NEVER be done by operators: Modifications of the tuning and matching network, especially of CP probes. Minor changes of the matching coil of X-wideline probe inserts can be done when followed by the WOBL procedure.

Chapter 7

Shim Coil

The effect of inhomogeneities on the spectrum is shown in Figure 7.1 .

The main field is homogenized over a certain region by different arrangements of the solenoid and saddle coils, which are affixed on the shim tube. Each coil is fed by its own power supply. The adjustment depends on the probehead, since the probehead can primarily generate field gradients of high order(z^3, z^4, z^5). Consequently, for each probehead, the optimal shim values must be found first. After the probehead is changed, the respective shim values must be readjusted. (For further data see Part f3)

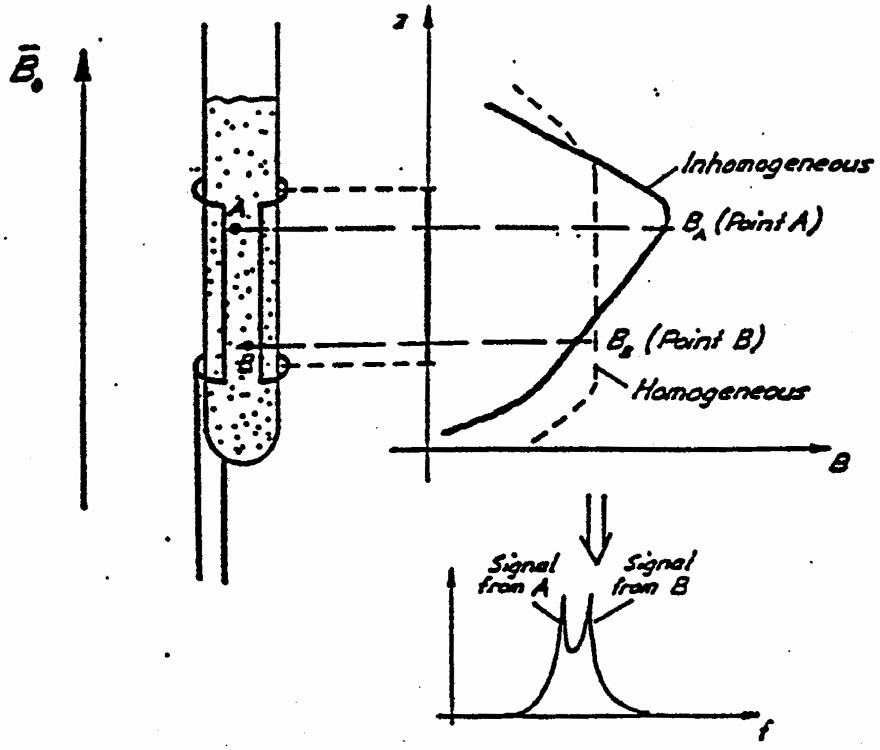


Figure 7.1: Effect of Field Inhomogeneities