Variable Temperature Unit

User manual VTU

Version 001

BRUKER

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Introduction to the temperature control 1

Introduction 1.1

For the majority of users the aim of temperature control is to remove the effect of any temperature fluctuations on NMR signals emitted by the sample. This is achieved by maintaining the sample at a constant temperature. Other users may therefore wish to study the effect of temperature changes on the sample and need to be able to vary the sample temperature in a controlled manner.

Overview of available units 1.2

Units in Basic System

1. BDTC, BVT3000 and BVT3300
2. Regulation heater
3. Temperature sensor : Thermocouple or PT100

Additional optional units

1. BCU05 Bruker Cooling Unit used for low temperature work. Sample temperatures down to 260-270 K can be achieved. The precise value will depend on the input air temperature as well as the type of probe and shim system.
2. Liquid Nitrogen (N_2) exchanger for very low temperature and 25 L dewar for very low temperature work. Sample temperatures as low as approximately 120 K are possible.
3. Liquid Nitrogen (N_2) heater and 25 L dewar for very low temperature work. Sample temperatures as low as 123 K approximately are possible.
4. BTO2000 BRUKER Thermal Oven for more accurate temperature control that 0.01 K might be required when using biological samples.
5. Venturi Pump : extends the minimum sample temperature by approximately 15 K for use with the BCU05.

Figure 1.1. Performance of temperature accessories

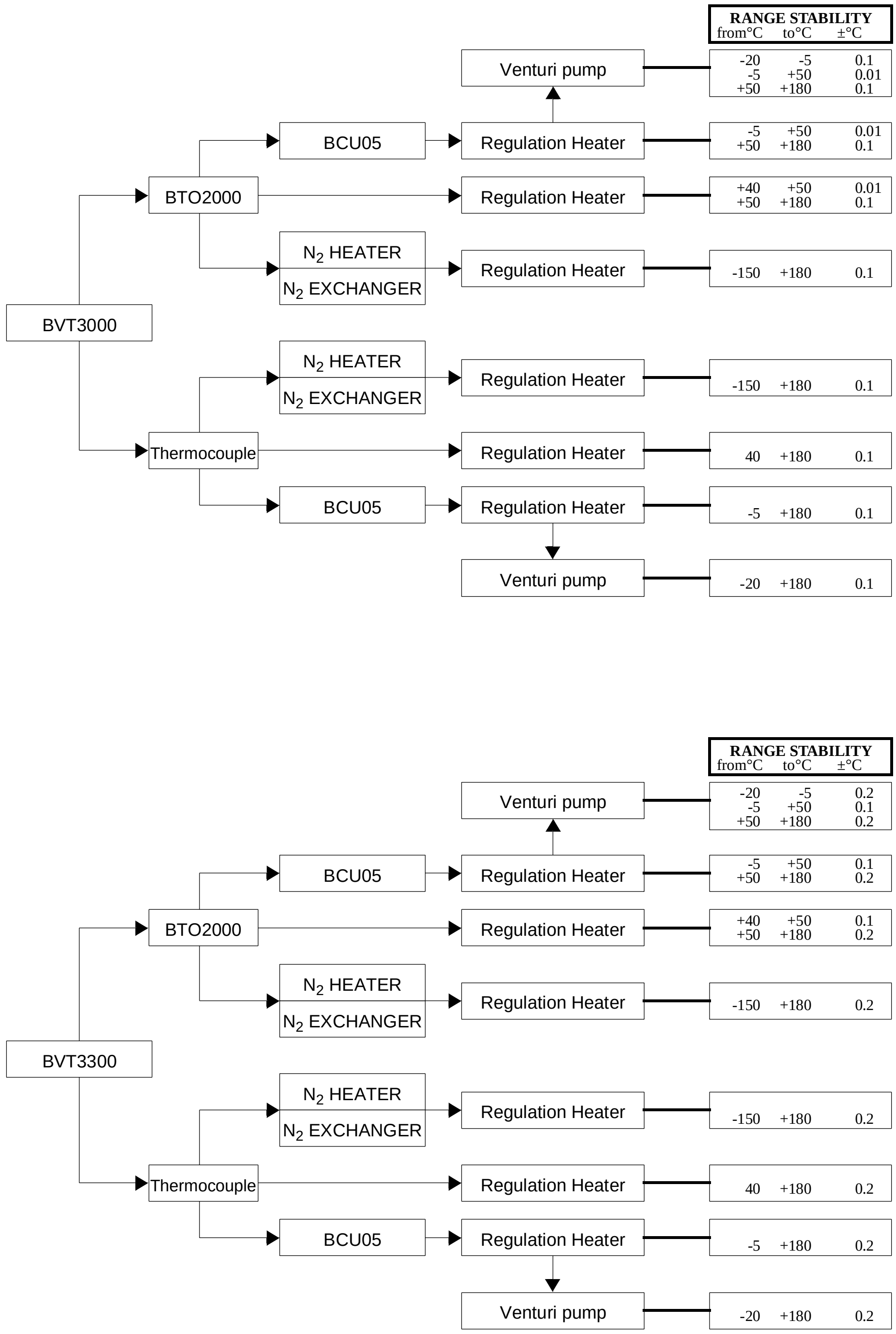


Figure 1.2. Temperature Control Units (Not to scale) W4M51634A

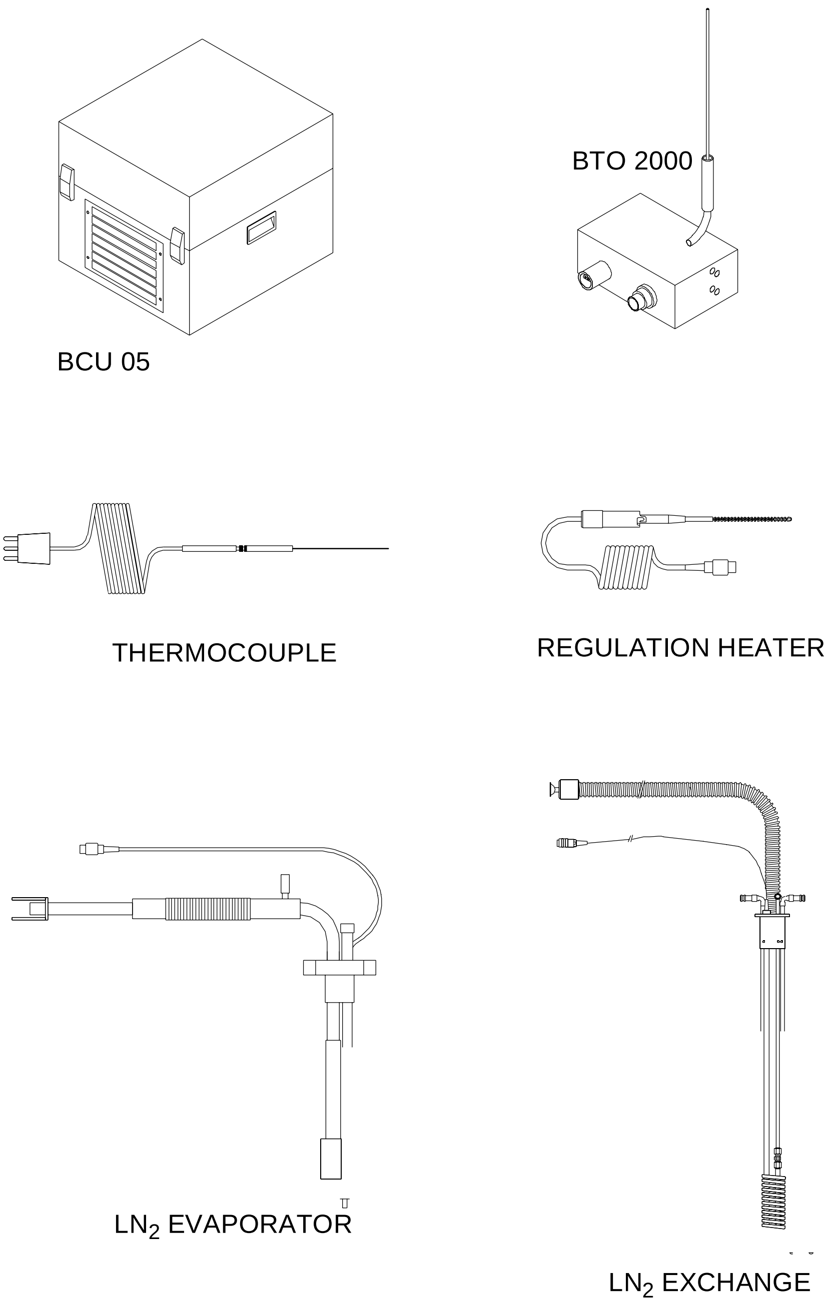


Figure 1.3. BDTC front panel

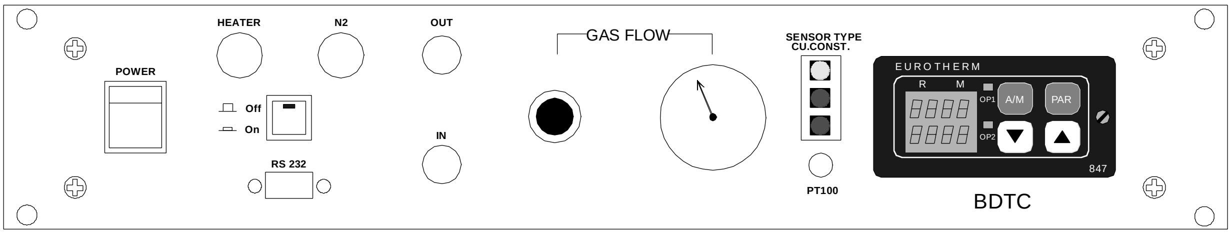


Figure 1.4. BVT3000 front panel

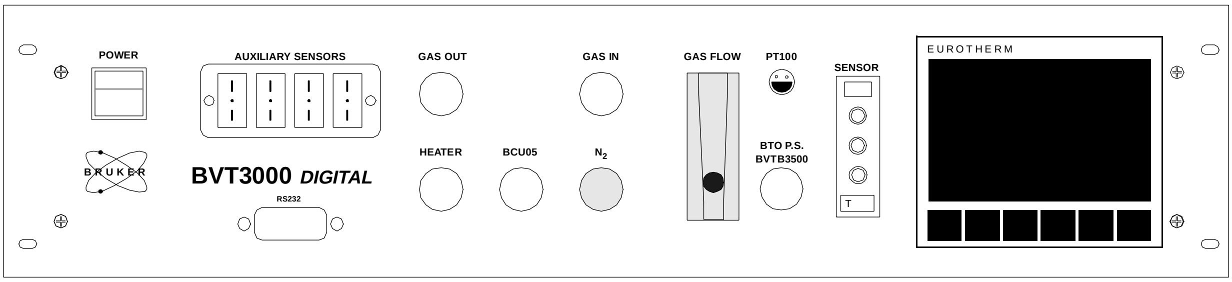
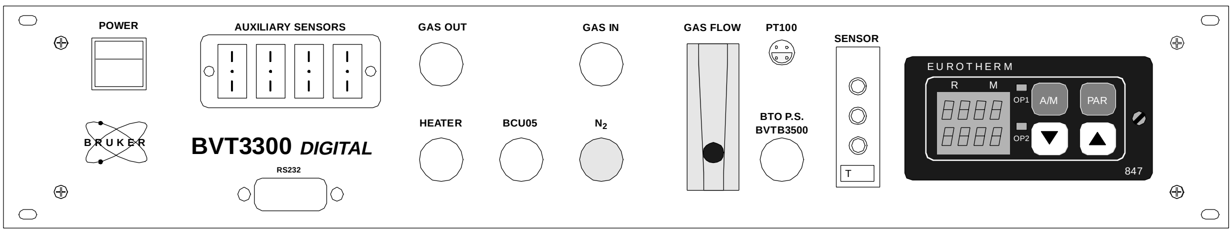


Figure 1.5. BVT3300 front panel



Operation of the basic system : room temperature work *1.3*

In order to be able to control the sample temperature it is normal to heat it (typically) 3-5 K above room temperature. The target temperature may be entered at the spectrometer keyboard.

Three connections are made at the base of the probe (see figure ***"Connecting Basic System" on page 14***

- Air flow :

  A stream of air is directed up through the probe and into the insert containing the NMR sample.

- Regulation heater :

  A heater inserted into the probe base warms the airflow before it reaches the sample.

- Thermocouple or PT100 :

  The temperature sensor measures the temperature of the airflow at a position typically 2-3 mm below the sample.

During normal operation the rate of air flow is constant. The temperature sensor measurements are analysed by the BDTC, BVT3000, BVT3300 and corresponding adjustments made to the regulation heater current. If the measured temperature is below the target temperature then the heater current is increased and vice versa. A regulation loop, programmed in the BDTC, BVT3000 and BVT3300, ensures that the control of the temperature is constantly optimized.

From the spectrometer keyboard it is possible to input a new target temperature. The BDTC, BVT3000 and BVT3300 will then adjust the heater current so that the target temperature is reached and stabilized as quickly as possible. Temperatures can be set and maintained to within ± 0.1 K. With this basic system it is possible to set the sample temperatures within the range from room temperature up to 473 K. For temperatures below room temperature additional accessories are required.

The BDTC, BVT3000 and BVT3300 are the control units of the regulation system and are described in figure ***"BVT3000 front panel" on page 20***

Figure 1.6.   Connecting Basic System

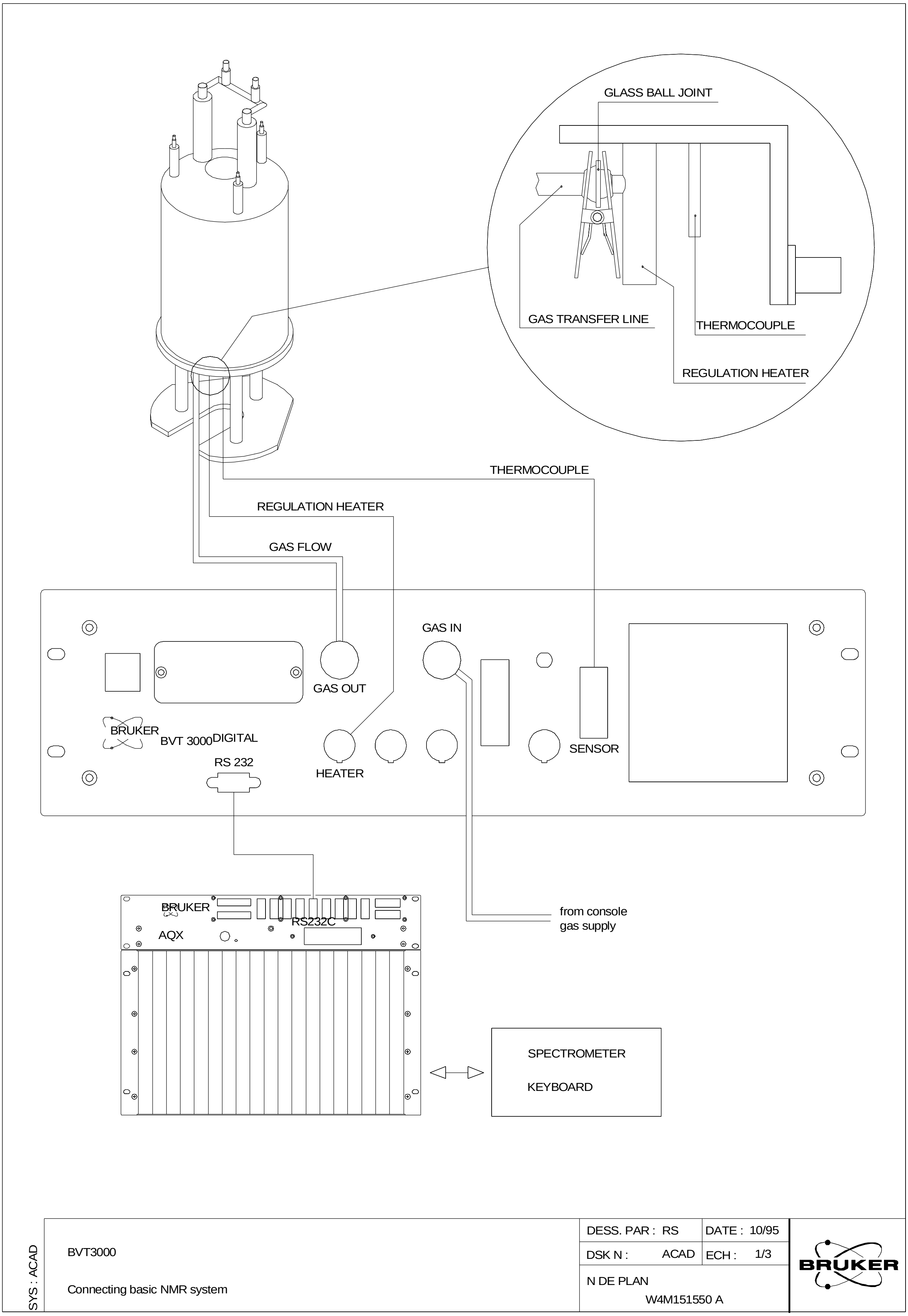
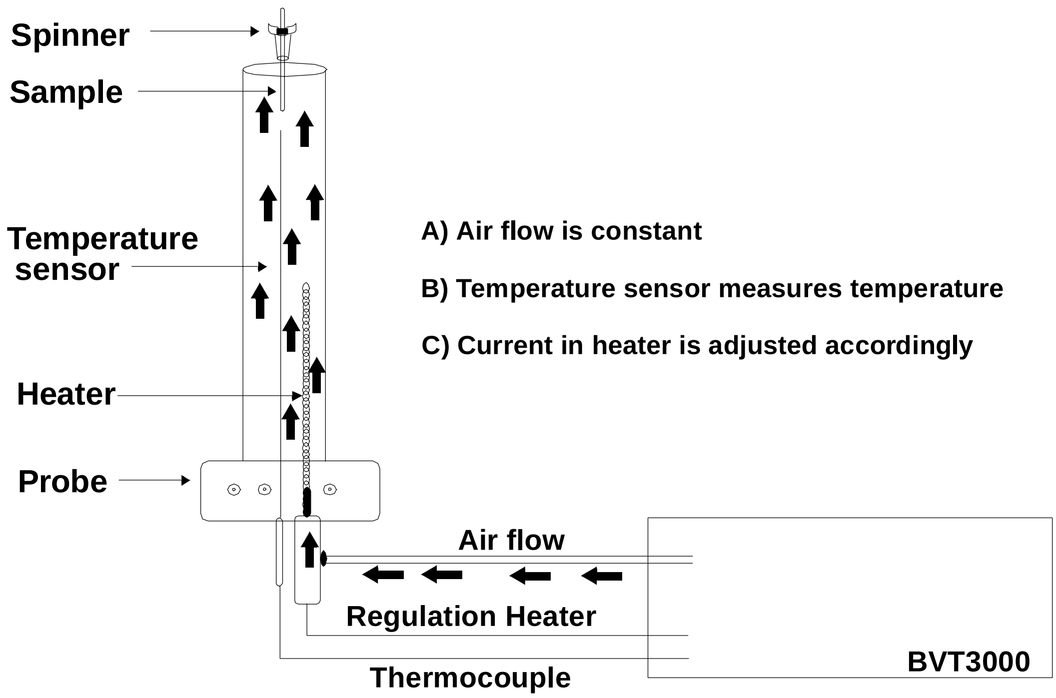


Figure 1.7. Basic principle of temperature control



BVT3000, BVT3300, BDTC

2

Principle functions 2.1

- Provide a voltage for the regulation heater. For low temperature work a liquid nitrogen (N_2) heater is also powered by the BDTC, BVT3000, BVT3300.
- Provide a connection to a suitable temperature sensor e.g. thermocouple or PT100.
- Regulate the air flow and controls the gas flow to the probe. For low temperature work this air flow can be used in the BCU05.
- Constantly monitors the probe temperature and makes appropriate adjustments to the regulation heater power.
- Remote control by the host computer.

For detailed informations, refer to :

- ***the BVT3000 Technical manual***
- ***the BVT3300 Technical manual***

Introduction to Front Panel Controls 2.2

Available controls on the front panel

- Eurotherm controller (type : 847, 902)
- Regulation heater connector.
- Liquid nitrogen (N_2) heater connector.
- Gas flow indicator.

Eurotherm 902 2.2.1

Position (7) measured temperature on figure ***"Eurotherm front panel (W4M110468)" on page 82***.

The large upper display is the current temperature in Kelvin as measured by the temperature sensor.

Position (11) secondary display on figure ***"Eurotherm front panel (W4M110468)" on page 82***.

The smaller lower display can be set to one of two options :

- SP : The value of the target temperature in Kelvin

- OP : The output power of the regulation heater as a percentage of maximum output.

The value of OP always refers to the regulation heater and never to the N_2 heater). You can choose which secondary display is operative by pressing the scroll button (as long as the keylock parameter in the “edte” table is set to “off”).

The Eurotherm controller can be controlled manually using keys on the front panel. A description of this control is given in chapter : ***"BVT3000 Manual Operation" on page 79***. However this is not the recommended mode of operation and the user is advised to use the Eurotherm controller as a display unit only.

Regulation heater control 2.2.2

The regulation heater may be turned on or off using the push button in XWIN-NMR command.

The OP parameter gives an approximate reading of the power in the heater as a percentage of maximum power.

☞ ***Note : The reading of this scale takes into account the heater power limit as set in the “edte” table e.g. if HO is set to 10 % and the needle reads 200 then this corresponds to 20 % of maximum power available in the unit.***

“PROBEHEAD OVERHEATING”

A thermocouple located within the regulation heater monitors the temperature. Should the temperature rise above certain preset limits, the “PROBEHEAD OVERHEATING” led will light and the heater will automatically switch off. When the heater cools it will automatically switch on again. However, you should always investigate the cause of such overheating, as it is not normal.

“GAS FLOW FAILURE”

If the airflow is cut off, then the regulation heater will automatically switch off.

You can easily simulate this by turning down the air flow rate.

Liquid nitrogen (N_2) heater control 2.2.3

This heater is used for low temperature work only and its control is explained in chapter : ***"Low temperature work with N2" on page 55***.

Gas flow indicator 2.2.4

A group of valves is used to set the rate of air flow. Typical values are 100 -2000 L/hour* as preset in the production departement. The precise value is not critical but once set it should not be altered. If the flow rate is altered then a new self-tune procedure (see the ***Edte User Manual***) should be carried out.

Power on/off switch (5) figure ***"BVT3000 front panel" on page 20***. Note that this switch will turn off all outputs from the BVT3000 including the air flow.

Controller configuration sequences are only required during initial configuration of the BVT. It's use is described in Chapter : ***"BVT3000 Manual Operation" on page 79***. (Configuration).

NOTE: The latest probes and BST unit allow flow rates of up to 1000 L/hour to be used.

The front panel — 2.3

On the front panel, you will find :

1: Auxiliary sensors (option BVT3000 and BVT3300)

2: Gas outlet

3: Gas inlet

4: Pt100 or BTO2000 connector

5: Power switch

6: RS232 connector

7: Heater connector

8: BCU05 connector

9: N_2 connector

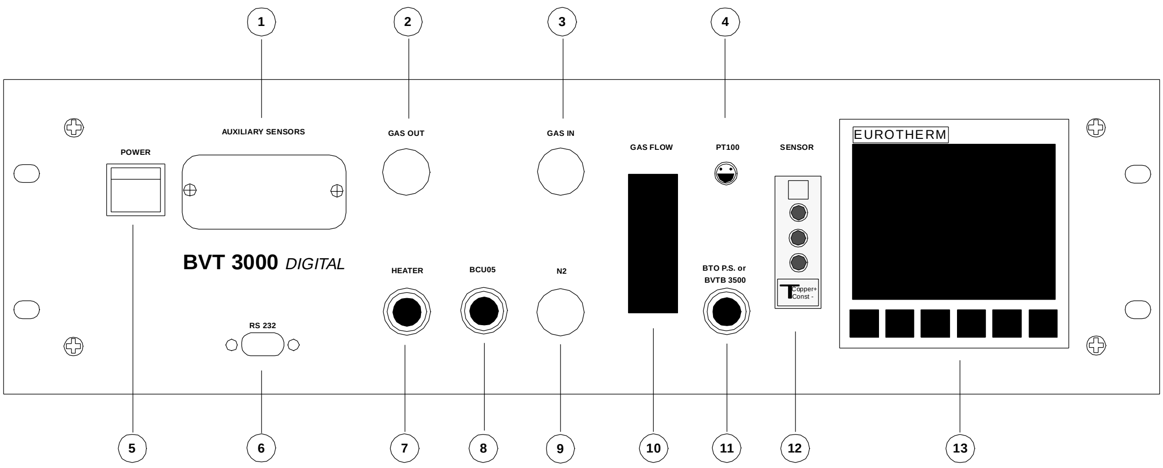
10: Gas flow indicator

11: BTO2000 power supply or BVTB 3500

12: Thermocouple connector type T

13: Eurotherm controller

Figure 2.1. BVT3000 front panel



Front panel connections 2.4

Heater connections :

The following heater connections are available :

- Position (7) labeled “HEATER” is a 7 pin socket for a regulation heater used for NMR systems. Standard power corresponds to 192 W and is the normal operating power. A 500 W power booster should only be used for very high temperature work (above 600 K) for which special probes are required.
- Position (9) labeled “N_2” is a 6 pin socket for an evaporator or an exchanger.

Temperature sensor connections :

Depending on the type of work to be done different temperature sensors may be connected (see chapter : ***"GasTemperature Sensors" on page 23*** for details of temperature sensors.)

Warning : never connect 2 different types of sensors at the same time.

- Position (12) is for thermocouple type **T** (Cu-CONST). This is the standard thermocouple used for NMR.
- Position (4) is for connection of PT100 or BTO2000.
- Position (1) is for auxiliary sensors.

Air flow 2.4.1

Position (3) : compressed air input. This input is taken directly from the main console air supply. This air must be sufficiently dry and free of dust and oil so as not to damage the probe.

Position (2) : air flow output. The air pressure is reduced to 0.3 bar within the BVT3000 and fed directly, or via the BCU05, to the probe base.

Computer connection 2.4.2

Position (6) is labeled RS232. The cable inserted here is an RS232 type cable and is connected to one of the tty ports on the SIB board of the spectrometer computer. This connection enables any commands entered at the spectrometer keyboard to be sent to the BVT3000 via the computer.

Position (11) is labeled “BTO PS or BVTB3500” If a BTO2000 is used then it is connected to this socket (see Chapter : ***"Bruker Thermal Oven BTO2000" on page 73***). If a Booster is used, it is connected on this socket in place of the BTO2000.

Technical specifications *2.5*

- Weight : 13 kg

- Dimensions (l x b x h) :

  483 mm x 461 mm x 130 mm (3U) for BVT3000

  483 mm x 461 mm x 86 mm (2U) for BVT3300

- Power supply

  220 V ± 10% : 50/60 Hz single phase

- Power consumption

  ca. 250 W

- Ambient temperature range 293 - 313 K

  Input air dry air with appropriate dew point[1] normally taken from air console supply. Pressure 4 - 6 bar

- Output air :

  Input air with pressure reduced to 0.3 bar

- Regulation heater power

  192 W at standard power

  500 W with booster (BVT3500)

- N_2 heater power (for evaporator)

  220 W

1. For room temperature work and higher : dew point < 277 K. For connection to BCU05 : dew point 223 K.

GasTemperature Sensors 3

Overview of available types 3.1

Table 3.1. Overview of available types

TYPE	T	PT100
MATERIAL	Copper/ Constantan	Platinium
TEMP RANGE K	73 - 623	73 -1123
TYPICAL APPLICATION	Standard NMR	

Thermocouple Type T 3.2

The standard thermocouple used in high resolution NMR is the type T thermocouple. The thermocouple position can be adjusted and is normally located 2-3 mm below the bottom of the sample tube. Therefore a small temperature gradient between the thermocouple temperature and the sample temperature exists. For a correctly positioned thermocouple this difference will be typically 1-3 K, though this will depend on the difference between the target temperature and room temperature. This is adequate for routine NMR where the sample temperature is kept constant and where precise sample temperature is not critical.

A good position of the thermocouple, however is very important if temperature studies are being carried out.

The effective length of the thermocouple and hence its position may be adjusted using the depth adjustment screw (1 turn = 0.5 mm). The brass extension rod (see figure ***"Thermocouple for HR probe (W4M151635A)" on page 25***) is designed to be used for probes up to and including 400 MHz. For 500 MHz magnets it should be removed. For 600, 750 and 800 MHz probes a special longer thermocouple is used.

Type K and E thermocouples 3.3

Table 3.2. Additional thermocouple types

TYPE	E	K
MATERIAL	Copper-Nickel	Nickel-Aluminium
TEMP RANGE (K) Intermittent use Continuous use	 273-1173 // //	 93-1623 273-1374
TYPICAL APPLICATION	High temp. NMR	High temp. NMR

If a system's probe(s) already contains these types of thermocouples or if experiments require high temperatures, the BVT3000 can be fitted with connection ports for E or K type thermocouples. This modification is made at the auxillary sensor port on the front panel of the unit (figure ***"BVT3000 front panel" on page 20***).

☞ ***Please note : systems using a EUROTHERM 847 microcontroller can accomodate type K thermocouples while type E thermocouples cannot be accomodated.***

Positioning the thermocouple 3.4

Method 1 : spinning rate 3.4.1

When using this method, care must be taken not to break the glass insert inside the probe.

1. Place a sample in the magnet and set the spin to “on”. Check the spinning rate and ensure that it is constant.
2. Slowly insert the thermocouple and continue to increase the thermocouple depth until the spinning is affected. The led “spin” on the SCM Storke BSMS keyboard will begin to blink. Determine the exact point at which the spinning begins to be affected.
3. Decrease the thermocouple depth by 2-3 mm.

Method 2 : visual inspection 3.4.2

With the probe removed from the magnet insert the thermocouple. The tip of the thermocouple may be seen using a small torch light. Adjust the thermocouple so that it is just above the bottom of the probe insert (see figure ***"Position of T thermocouple (W4M151636A)" on page 26***).

Using the same thermocouple with different probes — *3.4.3*

It may be necessary to adjust the probe itself so that the same thermocouple length may be used with several probes. This means that whenever a probe is changed, the thermocouple need not be lengthened or shortened. The effective length of the probe as seen by the thermocouple may be varied by adjusting the length of the insertion sleeve at the base of the probe. A special tool is required to make this adjustment and should be attempted by experienced personnel only. This adjustment is normal and needs only be done once.

Figure 3.1. Thermocouple for HR probe (W4M151635A)

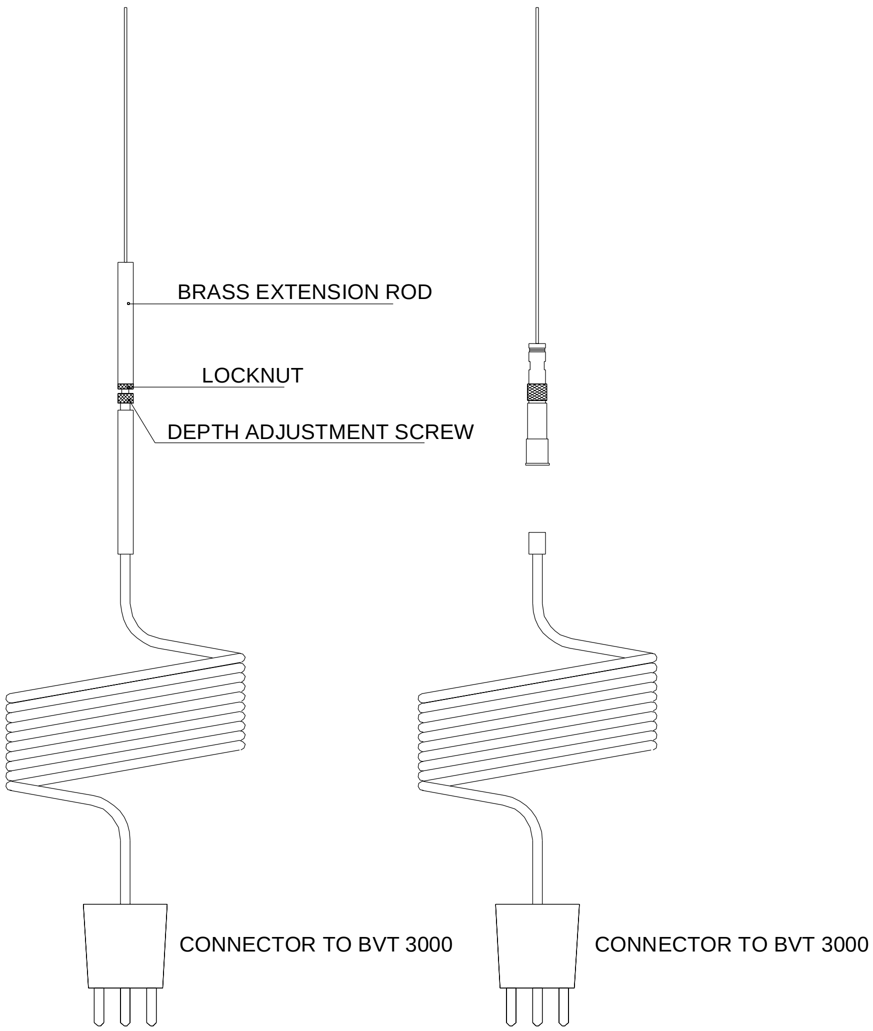
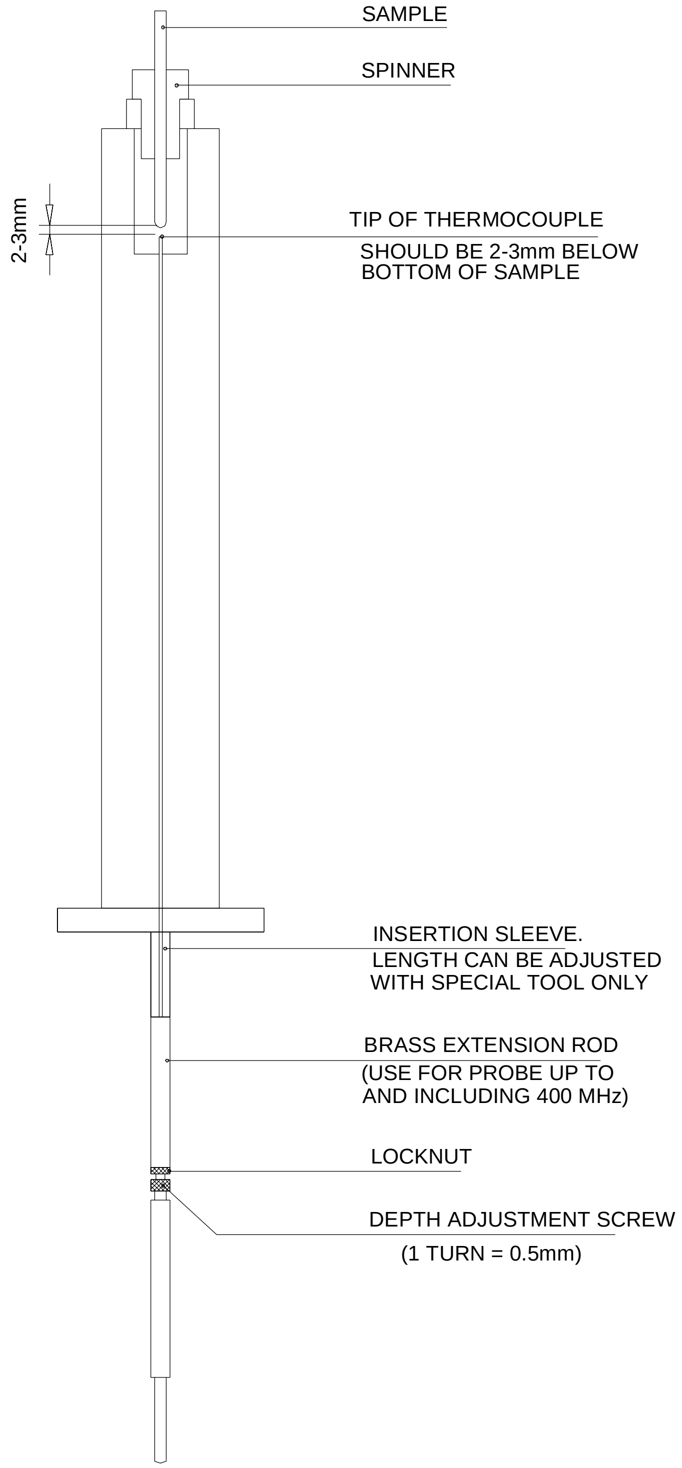


Figure 3.2. Position of T thermocouple (W4M151636A)



Effect of thermocouples on the shim values 3.5

Probes should always be shimmed with the heater and thermocouple already inserted. If this is not done, and a thermocouple is later inserted, then some reshimming may be necessary.

Thermocouples may have an adverse effect on the magnet homogeneity since they are ideally placed quite close to the sample. Older thermocouples (before 1986) contained enough magnetic material to require considerable re-shimming, possibly up to Z^4. More recent thermocouples have a titanium sheath and will only have an effect on the Z and Z^2 shims.

The presence of the regulation heater will have little or no effect on shimming since it is far enough from the sensitive area of the magnet.

Regulation heater 4

The heater should be left inserted in the probe even when not in use.

This heater operates on D.C. and is connected to the 7 pin socket labeled «heater» at the front panel of the BVT3000.

For NMR work sample temperatures of up to 470 K can be achieved with standard power.
Temperatures up to 900-1000 K are possible with the Booster (BVTB3500). This requires the use of special high temperature probes.

The same standard heater is used for all superconducting magnets up to and including 600 MHz frequency. The heater comprises a resistive wire wrapped around a central support containing a thermocouple. The safety thermocouple monitors the temperature of the heater itself. If, as a result of a fault, the heater should become too hot then it will automatically shut off while the "Edte display" will appear. The cut-off temperature will depend on the application and is set in the factory by adjustments made to the BVT3000.

For routine NMR the cut-off temperature is approximately 620 K.

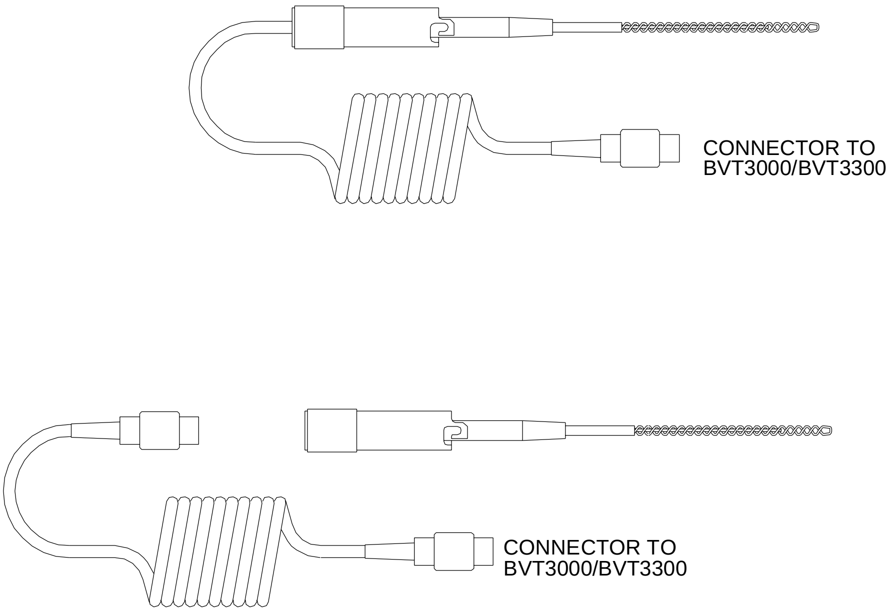
When the temperature drops below the cut-off temperature the heater will automatically switch on again but you should first check the cause of the overheating.

Should overheating occur with sufficient overshoot in temperature (e.g.a sudden loss of gas flow combined with high heater current) then the regulation heater may switch off completely. If this happens a relay is switched inside the BVT3000, this means that the heater will not automatically switch back on even after cooling. In such circumstances the heater must be turned on again manually in the «Edte display».

Positioning the heater *4.1*

No adjustment is necessary. Simply insert the heater into the base of the probe and lock it.

Figure 4.1. Regulation heater (M151637A)



Probes, spinners, sample tube performances

5

Probes 5.1

The following sections have been included to give an indication of the working temperature ranges of various probes. The range of temperatures will depend on the duration of the experiment. All of the temperature ranges quoted below are for standard NMR experiments typically lasting no longer than two hours.

For long term experiments, at extreme temperatures, the working range of the probe may be reduced. Special probes available from Bruker, are recommended for such experiments. If you have any questions regarding temperature specifications, then you should contact Bruker.

Standard probes 5.2

These probes are available in a wide range of designs e.g. broadband, selective, inverse, QNP, triple resonance, dual probes.

Variable temperature experiments are possible within the range of :

5 mm 123 K to 453 K

10 mm 143 K to 423 K

For long term experiments, at extreme temperatures, Bruker will provide a special heat/cooling flange.

Z gradient probes 5.3

Variable temperature experiments are possible within the range of :

223 K to 353 K

Low temperature probes 5.4

Two special types of probes are available which are recommended for long time experiments at very low temperatures.

Type A are designed for fast temperature changes or long term temperature experiments.

Type B are designed for small temperature gradients within the sample volume.

Variable temperature experiments are possible within the ranges :

Type A : 93 K to 453 K

Type B : 123 K to 453 K

In order to operate low temperature probes, a cooling system BVTE3900 is required. The system is used to prevent icing of the shim coil, probe and magnet dewar.

These probes are available in a wide range of designs such as broadband, selective, inverse, triple resonance, dual probes.

High temperature probes 5.5

Special types of probes are available which extend the maximum working temperature.

Variable temperature experiments are possible within the range :

123 K to 873 K

These probes are also versatile enough to be used for long term low temperature experiments for temperatures down to 153 K.

In order to operate high temperature probes, a cooling system BVTE3900 is required. The system is used to cool the shim coil, probe and magnet dewar.

High temperature probes are available as selective or dual probes.

Spinners 5.6

Three types of sample spinners are supplied with the spectrometer.

Plastic KEL-F (milky colour)

These spinners are suitable for spinner temperatures between 223 K and 323 K.

Plastic (blue colour)

These spinners are suitable for spinner temperatures between 223 K and 323 K. These spinners differ from Type A, in that they are less expensive and often used in automation. Plastic spinners are unsuitable at low temperatures, not because they shatter, but because they are too light for the N_2 gas flow.

Ceramic spinners :

These spinners are suitable for temperatures between 90 K and 450 K.

However, these spinners should not be used for standard room temperature work as there is a danger that tiny ceramic particles will be emitted during sample lift.

Sample Tubes 5.7

The standard sample tubes (Wilmad 513-1PP-7 and 507-PP-7) delivered by Bruker may be used for temperatures up to 510 K.

If higher temperatures are required then the use of quartz sample tubes should be investigated.

Calibration of the sample temperature 6

The temperature displayed on the Eurotherm controller front panel is the temperature measured by a temperature sensor positioned just below (typically 2-3 mm) the bottom of the sample tube. This will not necessarily correspond to the actual sample temperature. There is likely to be a temperature gradient within the probe insert, and so there will be a small difference between the measured temperature and the sample temperature.

➪ ***Note : For a stable system, with the temperature sensor optimally positioned, the difference between temperature sensor and sample temperature may be as little as 0.3 K for a target temperature of 300 K. If the temperature sensor is not correctly positioned then the difference could be as large as 5 K.***

For many users the precise value of the absolute temperature of the sample is not important as long as the temperature remains stable. However, if the absolute temperature is required then either of the following calibrations may be used.

The experiments described are very easy to perform and are also a quick check if you suspect that the temperature sensor is giving a false reading.

High temperature calibration *6.1*

Sample :

80 % Ethylene Glycol in DMSO-D_6 (Dimethyl Sulfoxide)

If this sample is unavailable then 100% Ethylene Glycol can be used with the lock switched off.

Experiment :

Observe ^1H, no decoupling

Temperature range :

300-420 K

Probe :

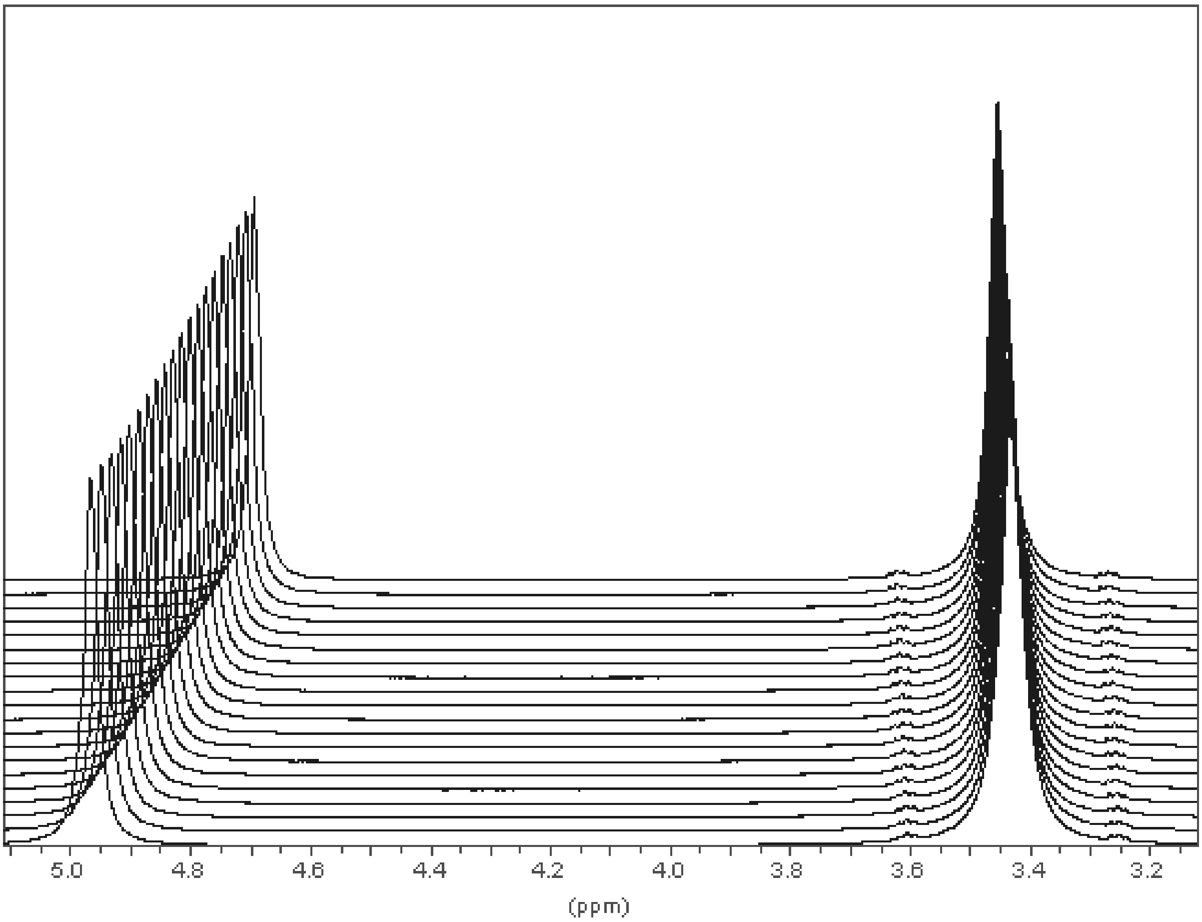
A ^1H selective probe is ideal though not necessary. The signal can easily be detected with a ^1H decoupling coil.

The spectrum displays two singlets corresponding to the CH2 and OH groups. The frequency difference between these two peaks is closely dependent on the temperature, and over a suitable temperature range can be represented by a straight line. Measure the difference in ppm. between the two singlets and use ***"Variable temperature calibration curve (for Glycol)" on page 38*** to determine the absolute temperature of the sample.

Alternatively use equations a) and b) listed below to calculate the temperature.

Equations a) and b) represent the two straight lines of ***"Variable temperature calibration curve (for Glycol)" on page 38***.

Figure 6.1. Glycol spectrum. Variable temp. 300 to 320 K by 1 K step



- a) 80 % Ethylene Glycol

$$T = \frac{(4{,}218 - \Delta\delta)}{0{,}009132} \qquad \text{(Eq. 6.1)}$$

- b) 100% Ethylene Glycol

$$T = \frac{(4{,}637 - \Delta\delta)}{0{,}009967} \qquad \text{(Eq. 6.2)}$$

where T = The sample temperature in degrees Kelvin

$\Delta\delta$ = Difference in ppm. between the CH_2 and OH singlets

Figure 6.2. Variable temperature calibration curve (for Glycol)

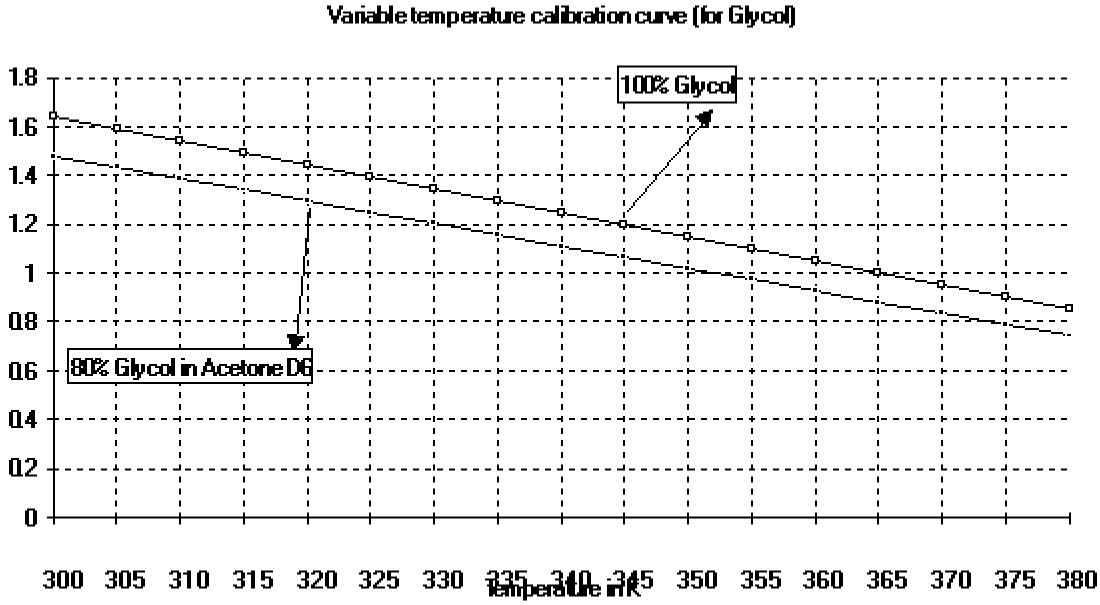
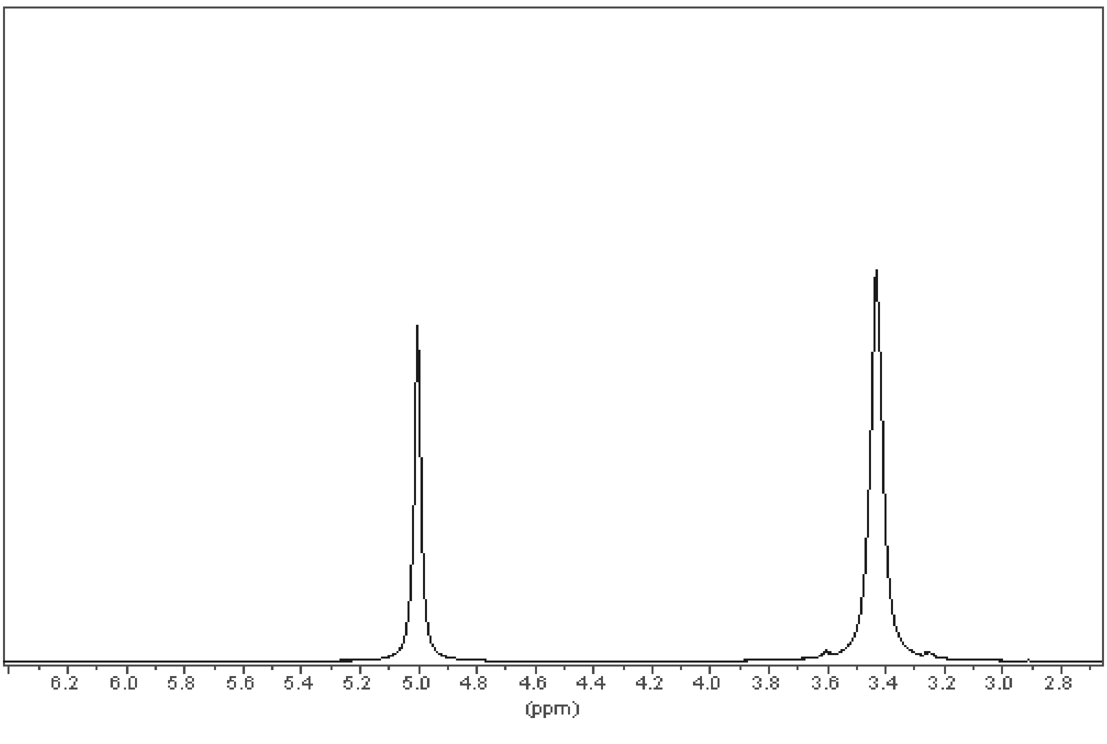


Figure 6.3. Glycol spectrum (80 % glycol in Acetone)



Low temperature calibration 6.2

Sample : 4 % Methanol in Methanol-D_4

If this sample is unavailable then 100% Methanol can be used with the lock switched off.

Experiment :

Observe ^1H, no decoupling

Temperature range :

180-300 K

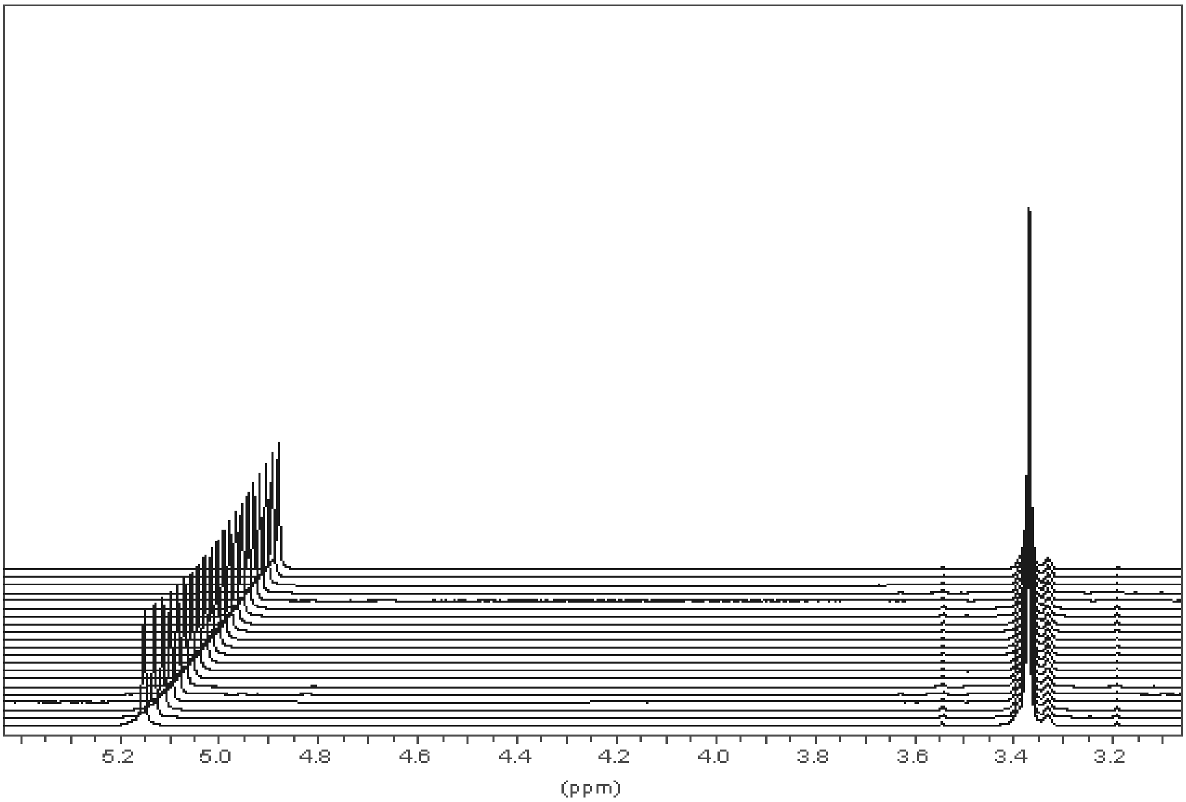
Probe :

A ^1H selective probe is ideal though the signal can easily be detected with a ^1H decoupling coil.

The spectrum displays two singlets corresponding to CH3 and OH groups. Determining the difference in ppm between the two singlets and the absolute temperature of the sample may be accomplished using figure ***"Variable temperature calibration curve (for Methanol)" on page 41***. Alternatively use equations c) through d) listed below to calculate the sample temperature.

Equations c) through d) represent the various linear section of ***"Variable temperature calibration curve (for Methanol)" on page 41***.

Figure 6.4. Methanol spectrum. Variable temp 180 to 300 K by 1 K step



- c) 4% Methanol in Methanol-D_4

Temperature Range (K)	Equation	
180 - 300	$T = (3.86 - \Delta\delta) / 0.00782$	(c)
180 - 230	$T = (3.72 - \Delta\delta) / 0.007143$	(d)
230 - 270	$T = (3.92 - \Delta\delta) / 0.008$	(e)
270 - 300	$T = (4.109 - \Delta\delta) / 0.008708$	(f)

- d) 100 % Methanol

Temperature Range (K)	Equation	
180 - 300	$T = - 23.832 (\Delta\delta)2 - 29.46 (\Delta\delta) + 403.0$	(g)

Please note : Although the expression for 100 % Methanol is best described by a second degree polynomial across the full, low temperature range, it can be resolved into three linear expressions covering smaller temperature ranges.

180 - 225	$T = (3.76 - \Delta\delta) / 0.007003$	(h)
220 - 270	$T = (3.99 - \Delta\delta) / 0.008001$	(i)
265 - 313	$T = (4.31 - \Delta\delta) / 0.009208$	(j)

Where T = the sample temperature (in Kelvin)

$\Delta\delta$ = the Difference (in ppm) between the CH_2 and OH singlets

Figure 6.5. Variable temperature calibration curve (for Methanol)

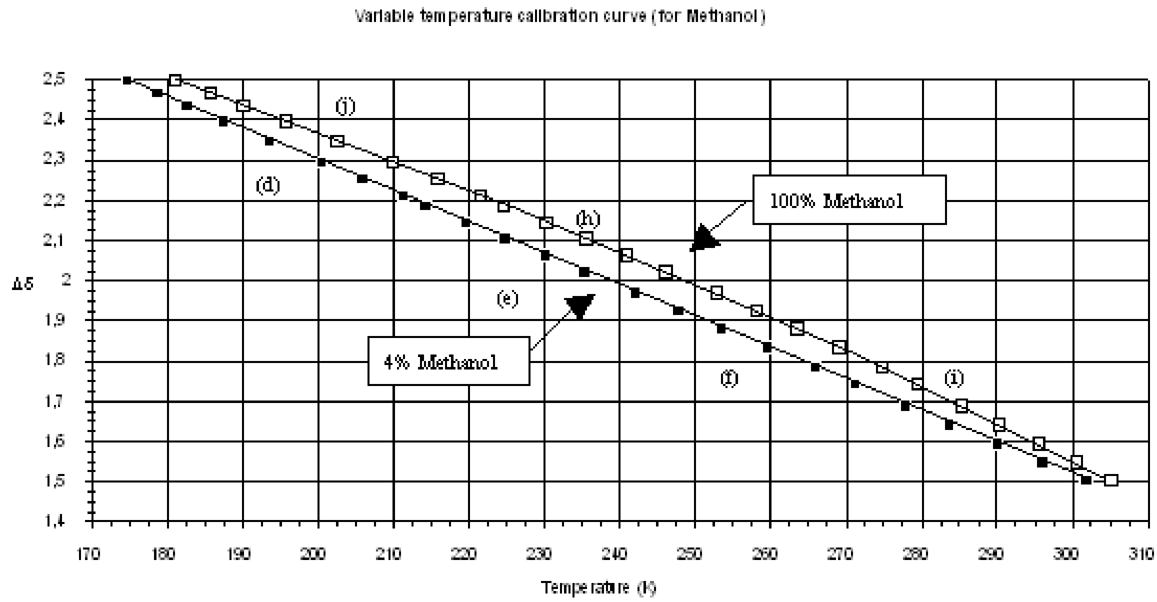
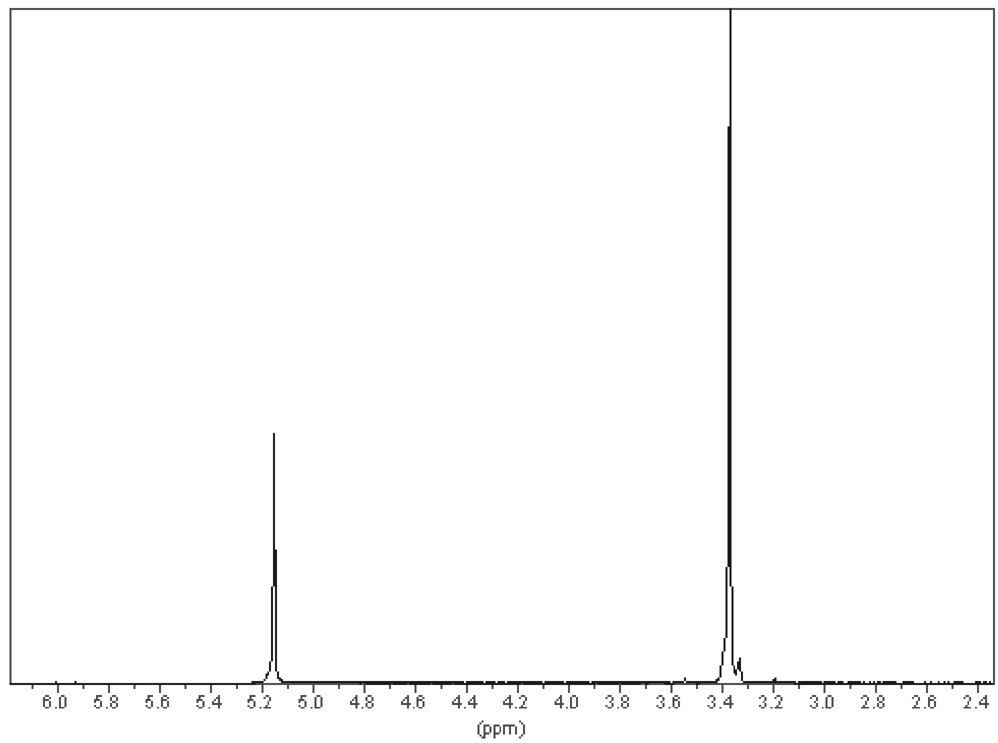


Figure 6.6. Methanol spectrum

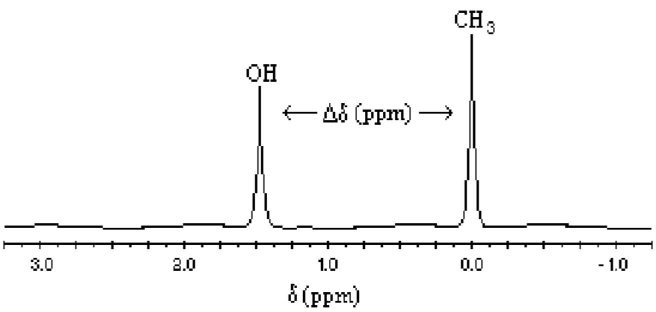


Temp. standardisation by NMR sample temp. measurement 6.3

Sample temperature is a predominant factor in the rates of most chemical processes and equilibria and for certain experiments must be known as precisely as possible. In the space between the NMR probe's temperature sensor and the NMR sample there exists a slight temperature gradient. This temperature gradient, a result of thermal conduction in the probe, is linear and creates a small offset between the target temperature ($T_{probe\ (^oK)}$) and the sample temperature ($T_{sample\ (^oK)}$). Temperature differences across this gradient must be accounted for so as to minimize experimental error.

A direct indication of the temperature within the spectrometer is the difference between the ^{1}H chemical shifts of the C-**H** and O-**H** peaks of methanol and/or ethylene glycol :

Figure 6.7. Typical methanol spectrum (target temperature ~ 300 K) showing C-H and O-H chemical shifts and the difference there between

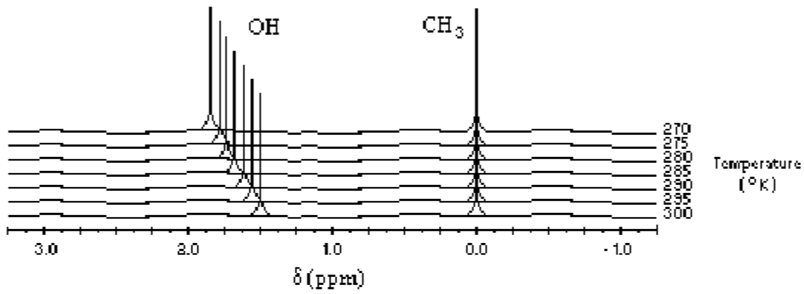


NOTE : The chemical shift axis in this diagram is expressed in parts per million (ppm), where :

$$\delta_{(ppm)} = v_{obs} / v_{ref} \times 10^6$$

The absolute value of this shift difference is inversely proportional to the sample temperature. At lower temperatures, hydrogen bonds increase thus, decreasing the (σ) electron density about the hydroxy proton. The net result is a desheilding effect which shifts the -OH proton's signal towards a lower field strength :

Figure 6.8. Combination of reproduced spectra of 4% Methanol in Methanol-D_4 observed in 5 degree increments from 270 - 300 K showing the increase in chemical shift difference corresponding to a decrease in temperature.



Statistical interpretation of these differences, obtained as a function of temperature, allows the target probe temperature and the temperature within the sample to be correlated.

- **i) Obtain spectra and quantify the difference in ^{1}H chemical shift (ppm) ($\Delta\delta$ (ppm)) of O-H and C-H in the appropriate standard(s) over the desired range of target probe temperatures.**

Typically, methanol chemical shifts are used for lower temperatures (ie. 180 to 300 K), while the chemical shift differences of ethylene glycol are used at higher temperatures (ie. 305 to 380 K). It is conveinient to use these products as standards as their physical properties (boiling and melting points) fall within the temperature ranges currently used in laboratories. Additionally, the nature of the protons in these standards gives rise to two singlets only, thus $\Delta\delta$ (ppm) quantification is not plagued by coupled signals.

Example : The chemical shift differences tabulated below were quantified from the spectra presented in figure ***"Combination of reproduced spectra of 4% Methanol in Methanol-D4 observed in 5 degree increments from 270 - 300 K showing the increase in chemical shift difference corresponding to a decrease in temperature." on page 43***. (4% Methanol in Methanol-D_4 recorded in 5 K increments from 270 to 300 K).

Point	Diff CS	T probe	Point	Diff CS	T probe
1	1.5	300	5	1.687	280
2	1.545	295	6	1.74	275
3	1.592	290	7	1.781	270
4	1.641	285			

- **ii) Determine sample temperature for each probe temperature using the $\Delta\delta$ (ppm) obtained and the appropriate linear relationship from the table below.**

Table 6.1. Tabulation of regression equations for ethylene glycol and methanol standards giving $T_{sample\ (K)}$ as a function of $\Delta\delta$

STANDARD	FONCTIONAL TEMP. RANGE (K)	REGRESSION EQUATION
100% Ethylene Glycol	300-380	$T(K) = -101.24\ (\Delta\delta) + 466.4$
80% Ethylene Glycol in DMSO-D_6	300-380	$T(K) = -108.33\ (\Delta\delta) + 460.41$
100% Methanol	180-300	$T(K) = -23.832\ (\Delta\delta)^2 + 29.46\ (\Delta\delta) + 403.0$
	180-225	$T(K) = -142.8\ (\Delta\delta) + 537.4$
	220-270	$T(K) = -124.98\ (\Delta\delta) + 498.4$
	265-313	$T(K) = -108.6\ (\Delta\delta) + 468.1$
4% Methanol in Methanol-D_4	180-300	$T(K) = -127.78\ (\Delta\delta) + 493.56$
	180-230	$T(K) = -140.0\ (\Delta\delta) + 521.33$
	230-270	$T(K) = -125.0\ (\Delta\delta) + 490.0$
	270-300	$T(K) = -114.83\ (\Delta\delta) + 471.85$

Note : The curve for 100% methanol is best described by a second degree polynomial across the full temperature range. However, this curve can be resolved into three linear expressions covering smaller temperature ranges.

The use of deuterated solvents (DMSO-D_6 and Methanol-D_4) allow a field lock to be applied, thus facilitating the quantification of chemical shift difference as temperatures change.

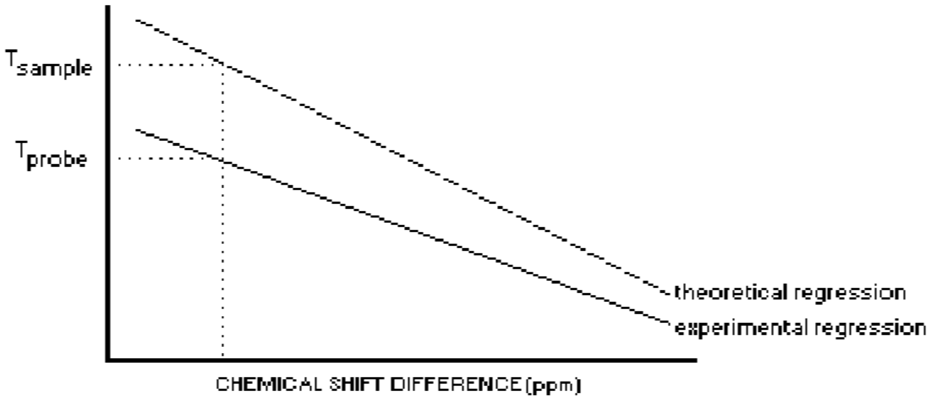
Example : Following the example above for 4% Methanol in Methanol-D_4 from 270 to 300 K, the appropriate equation in table ***"Tabulation of regression equations for ethylene glycol and methanol standards giving Tsample (K) as a function of Dd" on page 44*** for the conversion of chemical shift difference to sample temperature is :

$T(K) = -114.83\ (\Delta\delta) + 471.85$

Converted data are shown in ***"Modified calcal**.xls spreadsheet used to manipulate chemical shift data into linear calibration curves for both sample and probe temperature." on page 46***.

- **iii) Generation of linear (y = m (x) + b) equations for both probe temperature and sample temperature versus difference in chemical shift (ppm)**

Figure 6.9. Sample regression plot showing the inequivalent linear relationships between T_{sample} and T_{probe} as a function of chemical shift difference.



The linear expression for **sample temperature** stands as in figure ***"Sample regression plot showing the inequivalent linear relationships between Tsample and Tprobe as a function of chemical shift difference." on page 45*** :

$T_{sample\ (K)} = m\ (\Delta\delta_{\ (ppm)}) + b$

The linear expression for the **probe temperature** can be expressed using the following regression analysis :

$T_{probe\ (K)} = m'\ (\Delta\delta\ (ppm)) + b'$

With,

$$m' = \frac{n \times \sum \Delta\delta\ T_{probe\ (K)} - \sum \Delta\delta d \times \sum T_{probe\ (K)}}{n \times \sum \Delta\delta^2 - (\sum\Delta\delta)^2}$$

$$b' = \frac{\sum T_{probe\ (K)} \times \sum \Delta\delta^2 - \sum \Delta\delta \times \sum \Delta\delta\ T_{probe\ (K)}}{n \times \sum \Delta\delta^2 - (\sum\Delta\delta)^2}$$

Where,

$\Delta\delta$ = the chemical shift difference at a given ...

$T_{probe\ (K)}$ = probe temperature, and

n = the number of observed shift differences

NOTE : Microsoft Excel spreadsheets calcal.xls can be used to perform this regression analysis for any given data set ; calcal25.xls for 28 sets of up to 25 data points each, calcal99.xls for 4 sets of up to 99 data points each and/or calcalpl.xls for 2 sets of up to 250 data points each. These spreadsheets can modified to accommodate more sets and/or data points.**

Example : The linear expression generated for the probe temperature is

$T_{probe\ (K)} = -105.37\ (\Delta\delta) + 457.90$

1. Data manipulations are shown in table ***"Modified calcal**.xls spreadsheet used to manipulate chemical shift data into linear calibration curves for both sample and probe temperature." on page 46***.

*Table 6.2. Modified calcal**.xls spreadsheet used to manipulate chemical shift data into linear calibration curves for both sample and probe temperature.*

%	Etalon	Gamme H	Gamme B
4	**MeOH**	**300**	**270**

									theo (echan)	expr (sonde)
# Piq	Diff DC	T son	T ech	dDC T son	dDC Tech	dDC sq	(s dDC) sq			
1	1.5	300	299.605	450	449,4075	2,25		1	22737.71698	22868,09
2	1.545	295	294.43765	455.775	454.9061693	2.387025		2	22788.36895	22914.57
3	1.592	290	289.04064	461.68	460.1526989	2.534464		3	132.3693	132.3693
4	1.641	285	283.41397	467.685	465.0823248	2.692881		4	131.928296	131.928196
5	1.687	280	278.13179	472.36	469.2083297	2.845969		5	37517.48024	37725.2505
6	1.74	275	272.0458	478.5	473.359692	3.0276		6	37309.34532	37523.26882
7	1.781	270	267.33777	480.87	476.1285684	3.171961		7	132.3693	132.3693
								8	131.928196	131.928196
									m	m’
									-114.83	-105.3719758
									b	b’
									471.85	457.9003591
	SUM									
n=	11.486	1995	1984.01262	3266.87	3248.245283	18.9099	131.928196			
7										

- **iv) Correlate of sample temperature and probe temperature**

This operation is the simple combination of the linear equations, generated above, for sample temperature and probe temperature as a function of chemical shift difference :

$T_{sample\ (K)} = M \times T_{target\ (K)} + B$

(such that, $m \times \Delta\delta + b = M \times (m' \times \Delta\delta + b') + B$)

With, $M = m / m'$

$B = b - (m / m') \times b'$

Example : The table below (contained within the calcal**.xls spreadsheet) summaries the components of the linear equation relaying sample temperature to the target temperature of the probe. The overall expression for this equation is:

$T_{sample\ (K)} = 1.09 \times T_{target\ (K)} - 27.15$

Table 6.3. Tabulation of the components of the linear equation relaying sample temperature to the target temperature of the probe

SLOPE:
1,089758441
OFFSET:
-27,15078129

For information on the automation of this correlation process, please see the section regarding the **B**ruker **A**utomatic **T**emperature **MAN**aging system (**BATMAN**) in section (see ***the Edte User Manual***, ***BATMAN*** ''Bruker Adjustment Temperature MANagement'').

Biological temperature stability 6.4

Sample : 1M Hexacyanocobaltate in D20

Experiment : Observe ^{59}CO, no decoupling

Temperature range : 273 - 323 K

Probe :

A BBI probe is ideal although the signal can easily be detected. The relative sensitivity of ^{59}CO is 30 % of proton NMR sensitivity. Measuring the frequency shift gives you a precise view of the temperature stability of the sample.

1M Hexacyanocobaltate CO [CN] 6 Kz

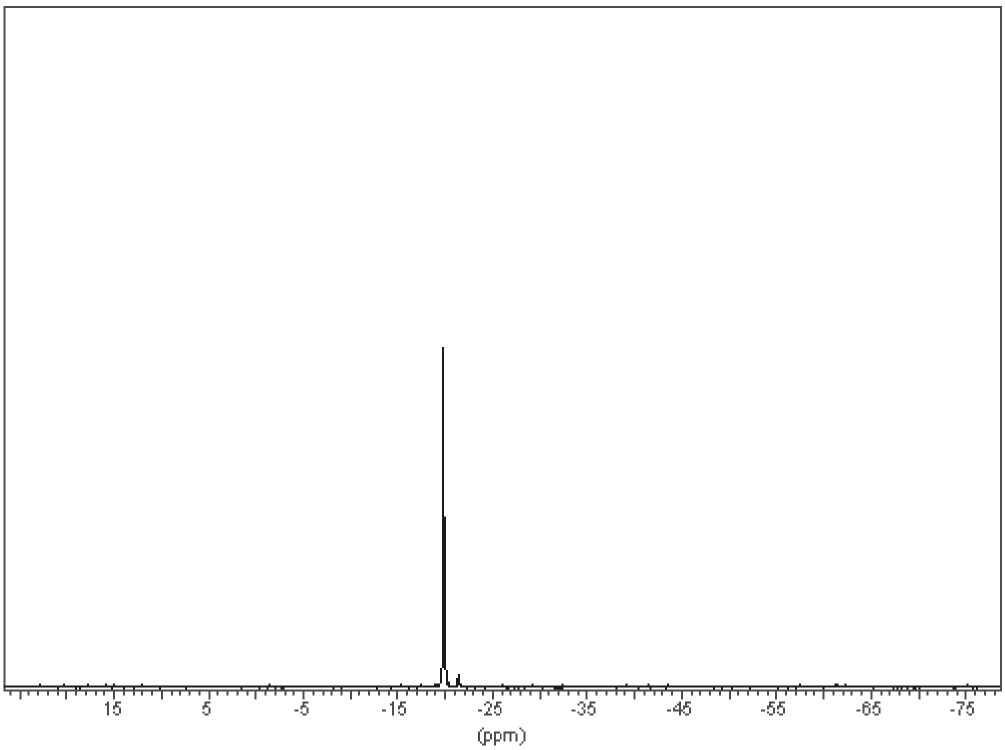
$$\Delta T = 1.40 \text{ ppm K} \times \Delta \delta \quad \text{(Eq. 6.3)}$$

where :

Δ T = Temperature shift in degrees Kelvin

Δ δ = Peak shift in ppm

Figure 6.10. Cobalt spectrum



AUtomated Spectrometer Operation

7

The ^{59}Co spectrum of $K_3Co\ (CN)_6$, Potassium Hexacyanocobaltate, is very simple in that it displays a single prominent peak that is easy to detect. The Cobalt frequency, however, has a strong temperature dependence with a frequency shift in the range of 1.4 ppm/K.

The precise frequency shift will depend on the sample concentration. Table 1 below lists the frequency shift for various magnets.

This sample is ideal to use as an example of an NMR temperature study. Two experiments could be carried out.

- The strong temperature dependence of the emitted signals could be used to measure the temperature stability of the system. Simply observe the frequency of the cobalt peak over a period of time and measure the size of frequency variations. With normal resolution, temperature shifts of ± 0.1K are easily detectable.
- Alternatively an automated program could be used to vary the temperature and measure the corresponding frequency shifts. Such an experiment will be described below as a typical example of a temperature study.

The AU program entitled “multizg” is designed to increment the experiment number for successive acquisitions. This allows a set of experiments under different conditions to be carried out. One experiment using the sample $K_3Co\ (CN)_6$ in D_2O, would be to vary the temperature automatically and carry out a set of acquisitions at different temperatures. The temperatures can be set automatically using a variable temperature list (VTlist). A peak picking on each transformed spectrum will then give the frequency of the Cobalt signal and in this way the temperature variations can be tracked.

To perform the experiment you will need to :

1. Set up the VTlist
2. Modify the multizg program.

Setting up a “VTlist” 7.1

Temperature lists are stored in the directory

/u/exp/stan/nmr/lists/vt

Each line of a temperature list contains one temperature only in degrees Kelvin.

To set up the temperature list use the following procedure :

1. Enter “edlist”
2. Click on “vt” with the mouse
3. Click on “Type new name”
4. Enter a name of your choice, e.g. “cobalt”
5. You will automatically enter the vi editor where you can make a list of temperatures, one per line.
6. Enter “eda” and click on the parameter entitled “VTlist”
7. Click the right mouse button and enter the required list e.g. "cobalt"

AU program 7.2

A copy of a suitable AU program is described below. It is a modified version of the AU program entitled “multizg” which is a standard Bruker AU program included in XWIN-NMR software.

```
/*
    multizg (900815)
    performs multiple acquisitions on increasing expnos.
*/char *Gets();
GETCURDATA
i1=atoi(Gets(“enter number of experiments :  “,”10"));
    RVTLIST
    TIMES(i1)
    VT
    TEREADY (300,0.1)
    ZG
    FT
    APK
    PP
    I EXPNO
    IVTLIST
ENDQUITMSG(“— AU program finished —”)
```

rvtlist :

The software reads the name of the list specified under “VTList” in the “eda” table and sets a pointer to the beginning of the list.

vt :

Set the temperature to the current position of the pointer.

teready (300.0.1) :

Wait until the set temperature has been reached. The two arguments to this command may be varied. The first argument (300) is the delay in seconds after the set temperature has been reached. The second argument determines the accuracy to which the set temperature is deemed to have been reached. Clearly the value assigned to both these arguments will depend very much on the required accuracy of the experiment.

zg :

perform an acquisition

ft :

Fourier Transform

apk :

Automatic phase correction.

Because of the temperature dependence of the signal there will be frequency variations as the sample temperature is varied. As such it is not possible to apply a single phase correction to various spectra. Therefore an automatic phase correction is performed separately on each spectrum.

pp :

Peak picking

The result of this AU program will be a set of spectra recorded at different temperatures. ***"Stackplot" on page 53*** is a stackplot of the recorded spectra of such an experiment. It shows clearly the temperature dependence of the Cobalt frequency.

Experiment details *7.3*

Sample :

$K_3Co(CN)_6$ in D_2O

Concentration :

1M

A solution of 247 mg of the sample in 1 ml of D_2O is suitable.

Experiment :

Observe ^{59}Co no decoupling

Probe :

The signal is quite strong so a broadband probe tuned to ^{59}Co is adequate. The spectra displayed in Fig. 8A were acquired with a 5 mm inverse broadband probe. A ^{13}C dual probe can also be used with the ^{13}C coil tuned to the ^{59}Co frequency.

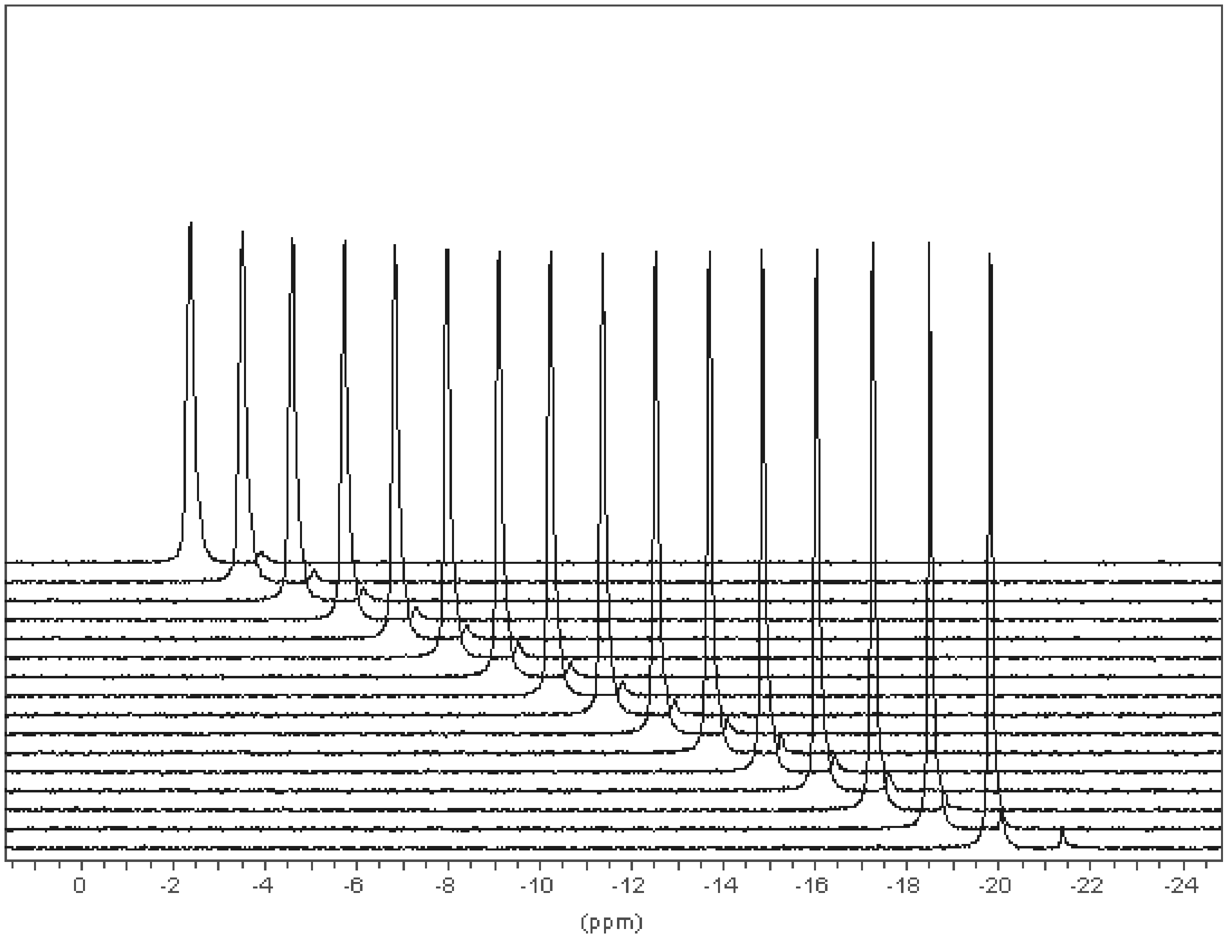
Resonance frequency at 300 K :

Resolution :

The Co line has a natural half width of 8 Hz. A half width of 10 Hz is readily achievable. Of course the accuracy of the experiment depends very much on resolution.

Figure 7.1. Stackplot

showing the frequency shift of Potassium Hexacyanocobaltate with temperature. Each plot represents a temperature shift of 1 Kelvin for the range 302 - 310 K.



Low temperature work with N_2 8

Introduction 8.1

The NMR sample may be cooled by a stream of cold nitrogen gas. The gas can be produced by evaporating liquid nitrogen using a heater immersed in a 25 L dewar. A second way to obtain a cold nitrogen gas is using a heat exchanger in 25 L dewar when you have nitrogen gas supply. An insulated transfer line carries the cold gas to the glass joint ball at the probe base. With this method sample temperatures as low as 123 K are achievable. The lowest sample temperature is determined by the cold gas flow rate rate set by the combination of the four valves in the temperature unit when you use a heat exchanger or by the evaporator heater power when the LN2 evaporator option is used. The higher the cold gas flow rate, the lower the sample temperature.

The heater current (0 to 100%) or the gas low rate may be adjusted in the «EDTE» software.

The use of the liquid nitrogen heater or N_2 gas flow control alone will not give adequate temperature control. It should always be used in conjunction with the regulation heater.

The suggested procedure is to use the nitrogen evaporator or heat exchanger to cool the sample to say 3-5 K below the proposed operating temperature. The regulation heater is then used to warm the gas by 3-5 K and maintain a steady temperature.

The precise operating conditions will depend very much on priorities. For a constant stable operating temperature it is sufficient to use the regulation heater to warm the nitrogen gas flow by no more than a few degrees. This reduces the consumption of liquid nitrogen. However if the temperature needs to be varied then the regulation heater will need to be used more, at the expense of liquid nitrogen consumption.

Safety Precautions 8.2

Working with cryogens such as liquid nitrogen represents a safety hazard. You should not use the N_2 heater until you are adequately aware of correct safety procedures.

- Avoid direct contact with liquid nitrogen or evaporated nitrogen
- Always wear safety goggles and protective gloves.
- Any open dewar of liquid nitrogen should be kept covered but not sealed.
- When transferring liquid nitrogen use suitable rubber hoses that do not splinter at low temperatures.

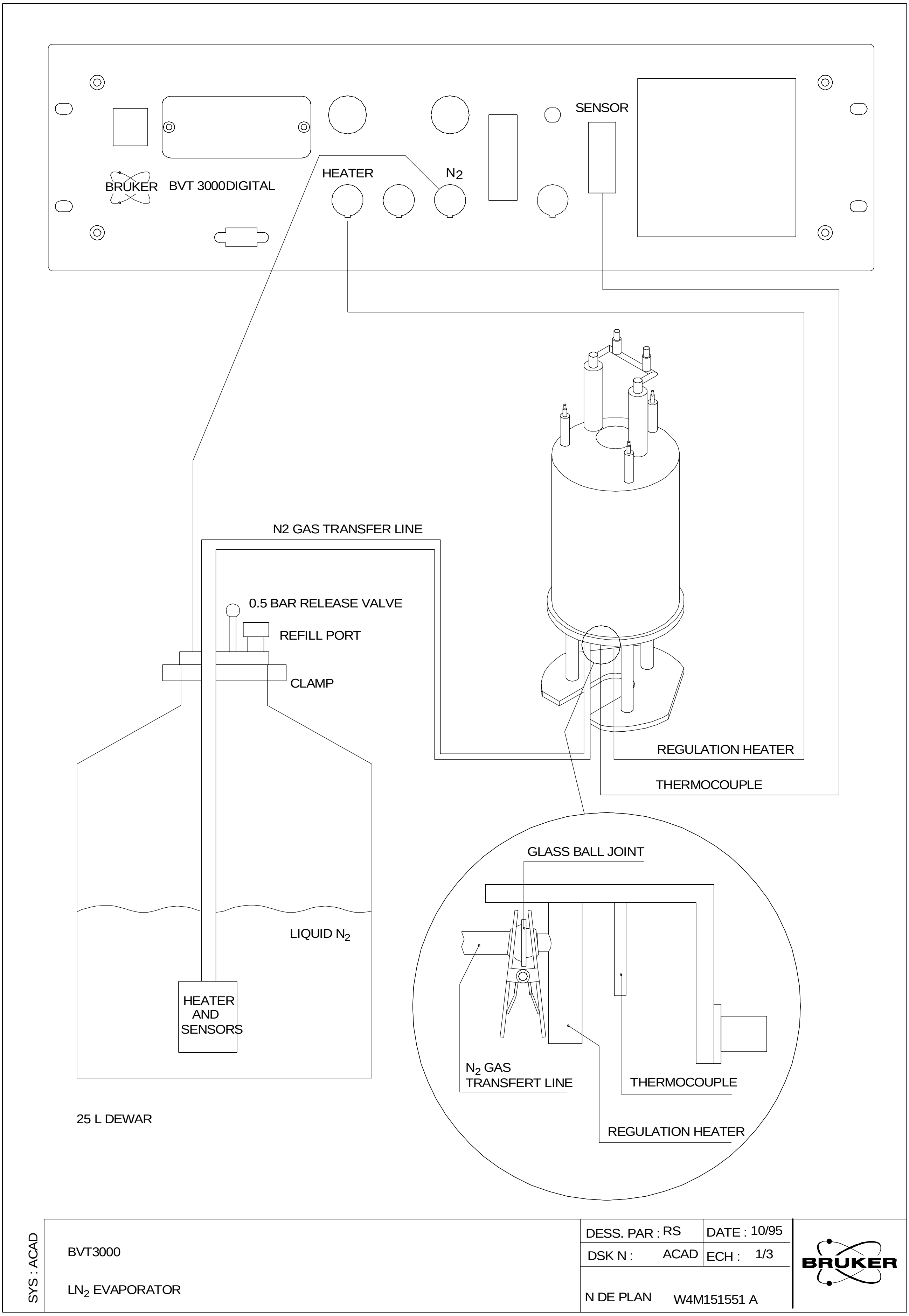
Construction and assembly 8.3

The N_2 heater is connected to the socket labeled N_2 at the front panel of the BVT3000. It is held in the 25 L dewar by a clamp. The user should note that this clamp contains magnetic parts. The dewar itself is made of non-magnetic material and can be operated close to the magnet.

Although the heater or the exchanger are relatively robust, for protection it is recommended that you leave then permanently clamped in the dewar, even when not in use.

The top of the evaporator assembly is fitted with a pressure release valve rated at 0.5 bar, as well as a refill port. In the case of the heat exchanger the pressure of the nitrogen dewar is the atmosphere pressure. When filling the dewar it is recommended that you use the refill port so that you do not need to remove the heater. It is recommended that you switch off the heater for a short period before refilling to allow the pressure in the dewar to drop.

Figure 8.1. Connecting the N_2 heater



Two types of transfer line are available. The standard black plastic line has a temperature gradient of approximately 30 to 40 K and is suitable for sample temperatures down to 123 K. This line is clamped directly to the glass ball joint at the base of the probehead.

For even lower temperatures, a steel transfer line with improved insulation (temperature gradient of 1K) is available. When using such a transfer line, it must be supported at the magnet by the clamp provided to avoid breaking the glass ball joint at the base of the probe. With this apparatus sample temperatures lower than 123 K are possible, but you need to verify that your probe is able to support this temperature.

The heater accessories contain a tube of silicon grease. This should be applied to the glass ball joint when attaching the transfer line. This will help seal the joints and prevent excessive icing at the joint.

Air supply for spinning — *8.4*

For room temperature work dry compressed air is normally used to spin the sample. At low temperatures any moisture in the compressed air will freeze. This can cause the sample to become trapped inside the probehead or the tuning mechanism of the probehead may be damaged. To avoid this the dew point of compressed air used to spin the sample should be at least 20 K below the proposed operating temperature. If suitable dry compressed air is not available for low temperature work, then dry nitrogen gas must be used to spin the sample.

Sample — *8.5*

Before starting any low temperature work ensure that the sample can withstand the low temperatures.

Operating procedure — *8.6*

1. Using “edte” set the sample temperature to the required operating temperature
2. Turn the regulation heater off and gas flow to minimum (or off).
3. Having filled the 25 L dewar and connected the gas transfer line, turn on the N_2 heater at the BVT3000 or set the power of the N_2 heater to a suitable value. If you use an exchanger, begin your experiment with a low gas flow. If you have never used the heater before, then you should begin at 10% of max. power and observe the drop in temperature. When the temperature has settled, vary the power and observe the temperature changes. This will give you a feel for the power required to achieve certain temperatures.
4. With the temperature at 3-5 K below sample temperature and reasonably stable, use the “edte” command to set “self-tune” to “on”.
5. Switch on the regulation heater. The Eurotherm controller will then perform a self-tune and then begin regulation.

Working with the N_2 heater *8.7*

The autonomy of 25 L dewar of liquid nitrogen depends on the heater current. Typically with the 50% output power, the heater can be operated for 8 hours.

The heater current can be set with the BVT3000 in «edte» window.

Two temperature sensors are built into the heater which define the “refill” and “empty” levels. The operation of these sensors is explained in figure ***"N2 heater temperature sensors" on page 59***.

Case 1:

> When sufficient liquid nitrogen is in the dewar, both sensors are cooled and the N_2 heater can be operated.

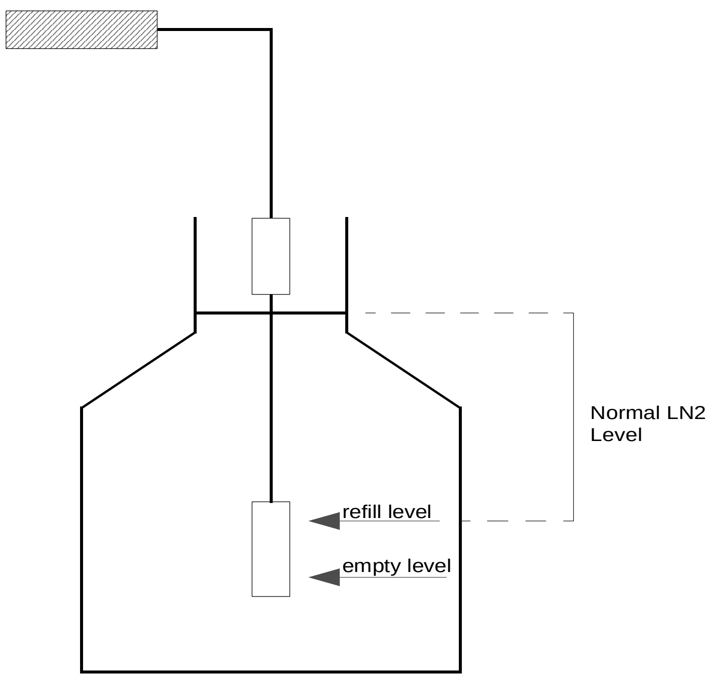
Case 2:

> When the level of liquid drops below the upper sensor triggers the “refill” level is indicated. When this happens the dewar should be refilled.

Case 3:

> If the liquid level sinks further a second, sensor becomes warm and triggers the “empty” level. When this happens the N_2 heater is automatically switched off. After refilling, the heater can only be started, it will automatically switch on again.

Figure 8.2. N_2 heater temperature sensors



BASM 9

Description 9.1

For detailed informations refer to ***the BASM Technical manual.***

The BASM **B**ruker **A**uxiliary **S**ensor **M**odule is an option module for a BVT3000 or BVT3300 temperature controller unit. The VTU's firmware must be version 2.1 or more recent.

It is designed for temperature monitoring only, not for sample temperature regulation. It has 4 inputs which can be for Pt100 or thermocouple.

The module is mounted on the front panel of the temperature unit.

Three modules with different inputs exist :

- W1101182 auxiliary sensor module with 4 Pt100.
- W1101183 auxiliary sensor module with 4 K thermocouple inputs.
- W1101184 auxiliary sensor module with 2 T thermocouple inputs and 2 E thermocouple inputs.

BVTB3500 10

Introduction 10.1

For detailed informations, refer to ***the BVTB3500 Technical manual***.

The BVTB3500 is a power booster unit for the digital temperature units BVT3000 and BVT3300. It allows to increase the heating power up to 500 watts. This product is useful for high temperature experiment in NMR or ESR.

This unit is fully controlled by a driving unit temperature.The electronics provides the power to the heater according a command signal issued by the BVT3X00. It can drive heater resistance from 6 to 12 ohms.

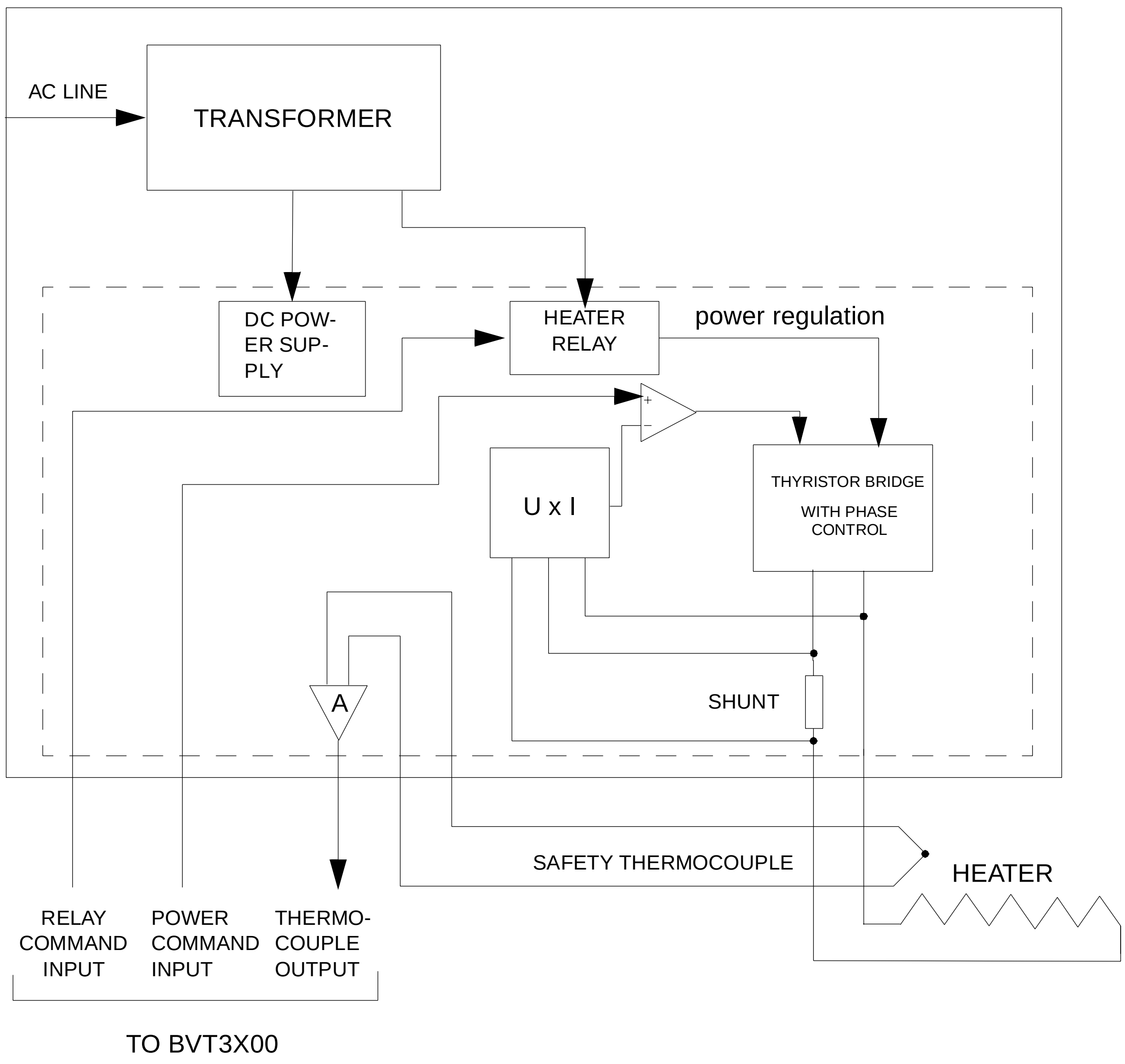
When the BVT3500 is activated the power stage of the driving unit is disabled.

System requirements 10.2

In order to use this product successfully, the following are recommended as a minimum:

1. a BVT3000 or a BVT3300 temperature unit is required.
2. a cable to link BVT3X00 and BVTB3500 (P/N W1101105).
3. a 500 Watt heater.

Figure 10.1. BVTB3500 block diagram



BVTE3900 11

Introduction 11.1

For detailed informations refer to ***the BVTE3900 Technical manual.***

The BVTE3900 (P/N W1208962) is a cooling system for high temperature NMR probes.

It works in conjunction with a temperature controller (BVT3000 or BVT2000) with an «E» thermocouple input, and allows to work at high temperature (above 150 °C).

It can be used as well for standard or even low temperature.

The system has a cooling circuit, power electronics and safeties.

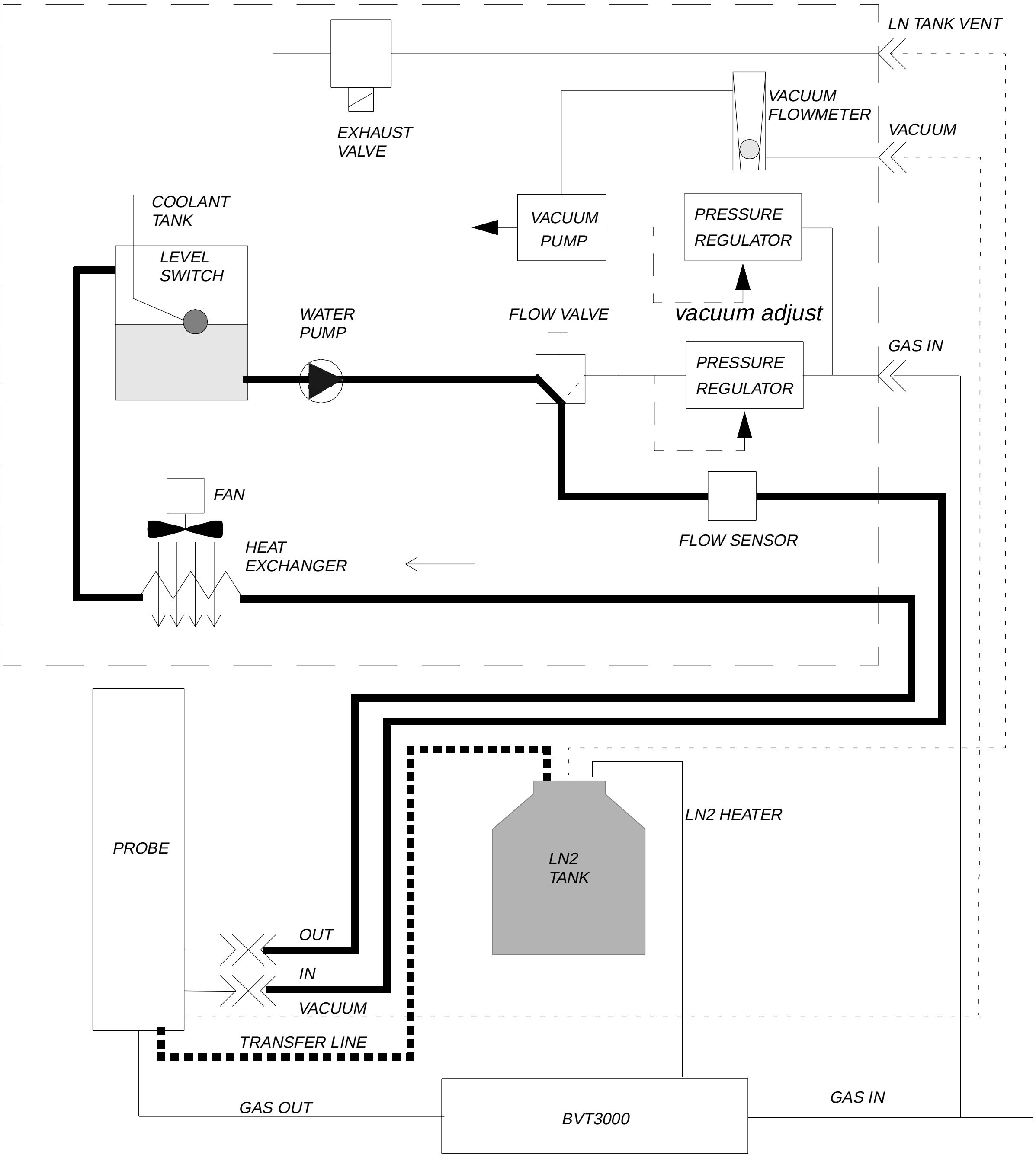
The cooling system comprises a cooling liquid tank and a circulating pump and safeties to prevent probe overheating.

The power electronics is mainly composed by a power booster driven by the digital temperature unit BVT3000.This unit is fully controlled by the driving unit temperature unit. The power electronics provides the power to the heater according a command signal issued by the BVT3000. When the BVTE3900 is connected to the BVT3000 and switched on the power stage of the VTU is disabled.

The power booster is by-passed when used with BVT2000.

A special version of the BVTE3900 called BVTE3900 LTE (P/N : W1209799) is available.
It is intended only for low temperature applications. This system avoids freezing of the probe housing. It works with a BVT3000 or a BVT2000.

Figure 11.1. BVTB3900 Liquid and gas circuit



Technical specifications 11.2

Table 11.1. Specifications

Heater power	500 W maximum
Heater resistance	8 ohms
Driving unit	BVT3000 or BVT2000 with «E» thermocouple input
Weight	60 Kg for basic system
Dimensions	560 mm (W) x 500 mm (H) x 560 mm (D) aluminium case
Voltage requirements	220 V + / - 10%, 50/60 Hz 6.3 A fuses on mains
Power consumption	220V/5 amp maximum at full heating power
Operating temperature	0 to 50 °C
Gas supply	4 to 10 bar compressed air 750 l/h at 4 bar compressed air for 500l/h suction
N2 gas supply	500 l/h for heating

Bruker Cooling Unit BCU05 12

Operating principle 12.1

For detailed informations, refer to ***the BCU05 Technical manual***

The BCU05 is a cooling unit that reduces the temperature of an air input by typically 65°C.

Freon gas is circulating around an external heat exchanger within a completely sealed system. The unit is designed to be operated in conjunction with the BVT2000 or BVT3000/3300. The VTU provides the gas input for the BCU05 as well as controlling the sample temperature. When operated in conjunction with a BTO2000, sample temperature stability of ± 0.01°C/°C can be achieved (with BVT2000 or BVT3000).

Operating notes 12.2

1. The BCU05 is be powered by the BVT3000/3300 and is designed for 24 hours a day operation as long as the probe is not exchanged. If the probe is to be exchanged then switch off the unit and wait for 10 minutes before handling. The exchanger tip must be de-iced before connecting on probe. Put vacuum grease on glass ball joint.
2. Never operate the unit without first gas flowing through the heat exchanger. Otherwise ice may form and clog the heat exchanger. The input gas should be dry, oilless and dust free if not serious damage to the probe may result.
3. The BCU05 is designed to take its gas input from the BVT2000, or BVT3000/3300.
4. Output :The temperature of the output gas is not directly controllable. Its temperature will depend on :

   a) The input gas temperature

   b) The ambient room temperature

   c) The throughput i.e. flow rate.

   If any of the above vary, then so also will the output temperature.
5. Sample temperature range: The BCU05 guarantees to cool the sample within the magnet to at least -5°C for a room temperature of 25°C. Slightly lower temperatures may be possible depending upon the type of probe, input air temperature, room temperature.
6. Location: The BCU05 is designed to be positioned at approximately 2m from the magnet probe.

7. Dew point : for an input air and room temperature of 20°C the output temperature will be approximately -45°C. To avoid freezing/ice formation the input air dew point should be at least -50°C.

Technical specifications 12.3

Sample temperature range	-5°C to + 50°C
Input :	
Taken from BVT2000 or BVT3000/3300	
• Dry air	(dew point < - 50°C) or dry N_2
• Pressure	0,3 bar
• Flow Rate	300-2000 l/h (Probe dependant)
Ambient temperature range	20 to 32 °C
Mains connection	1x 208/220/240 Vac - 50/60 Hz - 450 Watts
Warm-up time	1/2 hour
Case dimensions	550 x 500 x 490 mm
Trump lenght	3 meters
Weight	
• BCU05	35 kg
• BCU05 LT	46 kg
Gas content	0,4 kg Freon R404A

Output

Cooled air or N_2 with temperature reduced by approx. 65°C.

Stability of output temperature

± 1°C under perfectly constant conditions of mains voltage, room temperature, air flow, etc.

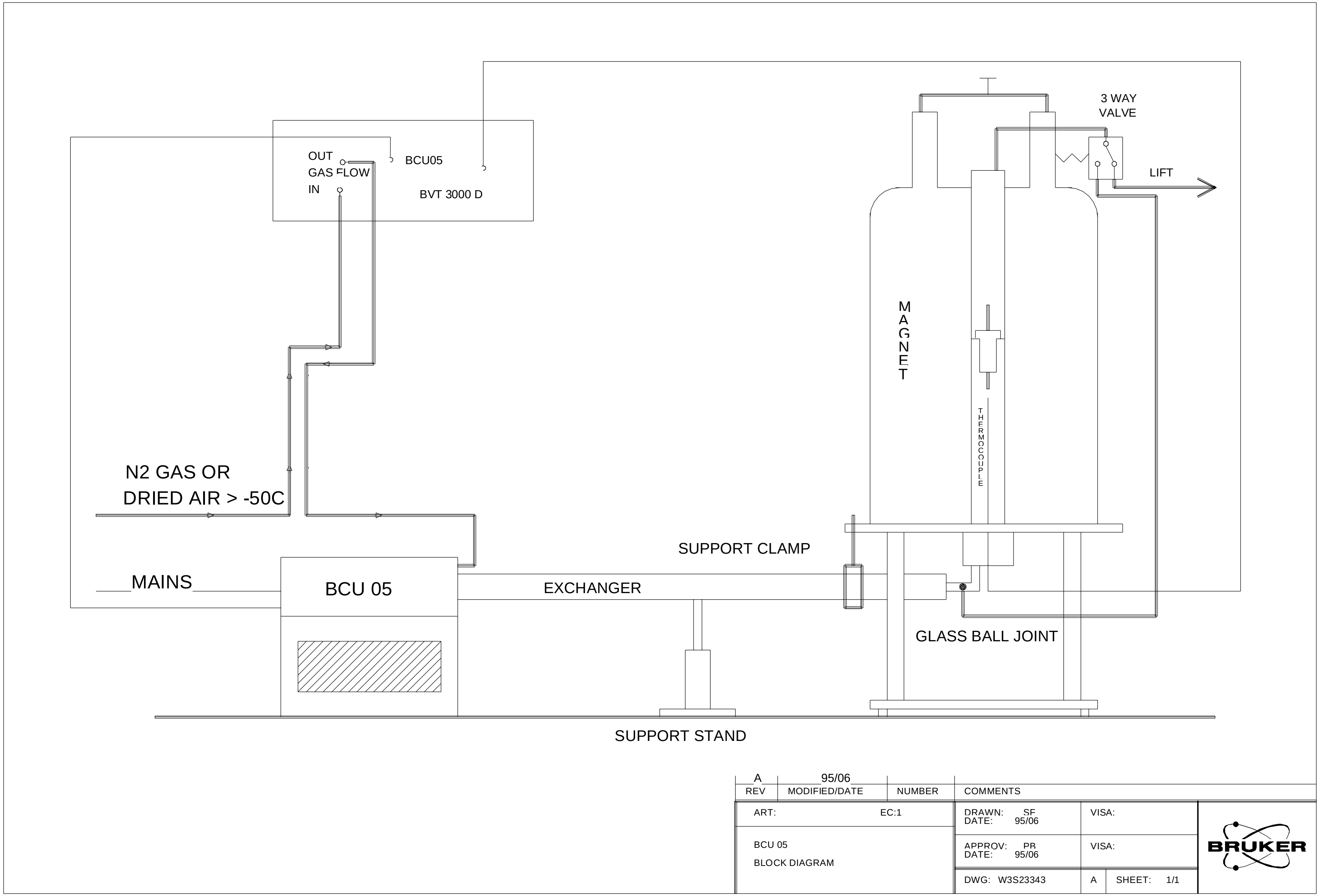


Figure 12.1. Connecting the BCU05 (W3S23343A)

Bruker Thermal Oven BTO2000 13

Operating Principle 13.1

The metal sheathed thermocouple probe has wires that are continued under the magnet by soldered thermocouple extension wires.

Because the composition of both wires can slighly differ, this junction is sensitive to room temperature variation and add a small error voltage to the thermocouple voltage.

The measure of the ratio of the charge of the sample temperature to the room temperature is called the Drif Temperature Coefficient (DTC). A standard T (Cu/Const) with extension wires can have a DTC as high as 0.1 K/K.

The BTO2000 achieves its improved DTC (< 0.01K/K) by maintaining the temperature of the cold junction at constant temperature in a small oven.

A special sensor located near the cold junction measures the oven temperature and removes any error signal coming from room temperature variation.

The BTO2000 is powered by the temperature unit.

➪ ***The BTO2000 may be ordered with the following thermocouples :***

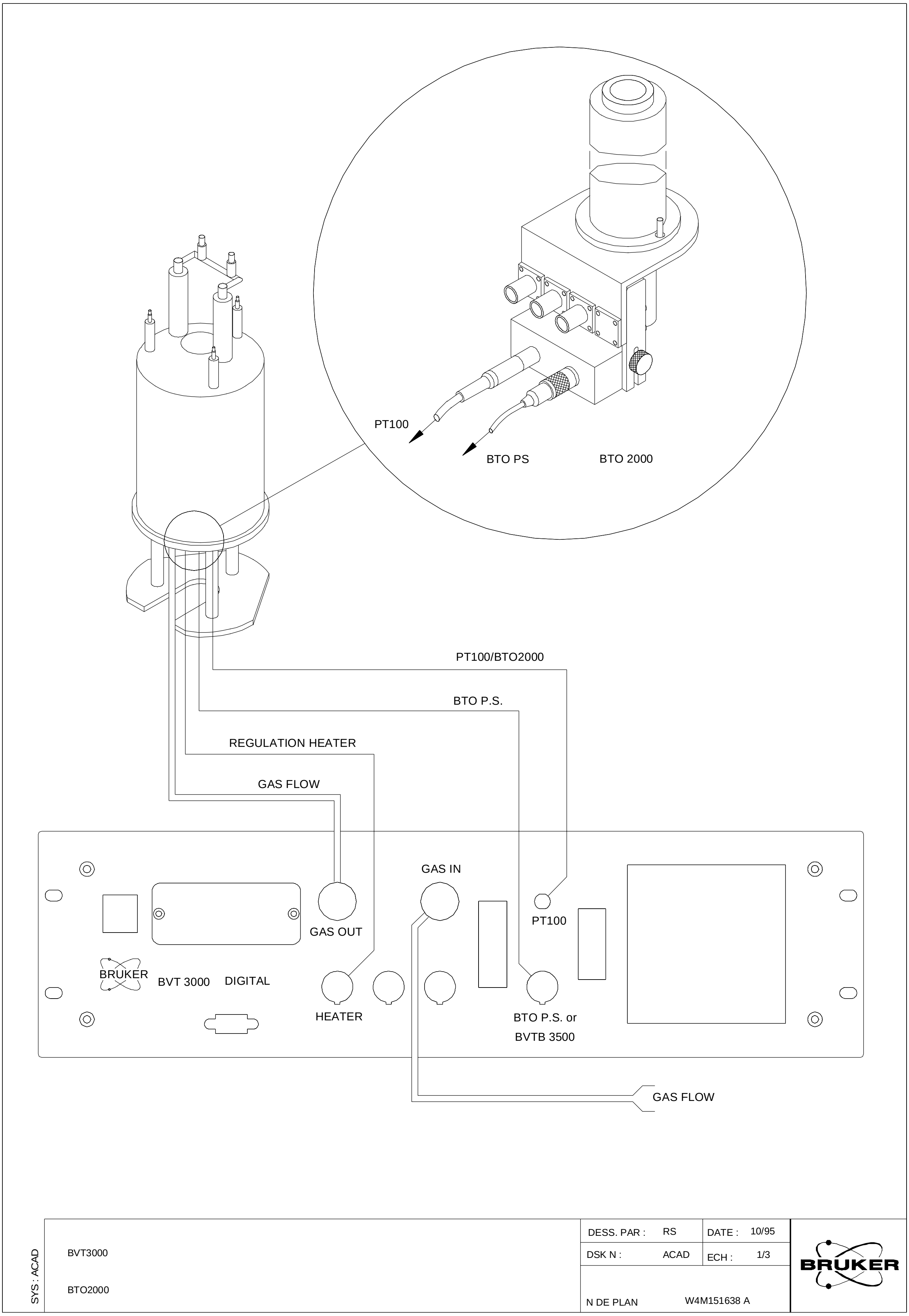
- Thermocouple type T Cu/Const suitable for NMR (standard model)
- Thermocouple type K CH/Alumel suitable for EPR
- Thermocouple type E CH/Const for high temperature work

The BTO2000 is delivered with the thermocouple already mounted and is simply fitted to the base of the probehead.

Technical Specifications 13.2

Power Supply (Provided by Temperature Unit)	+15V/200mA max.
Drift Temperature Coefficient (room temp. 288 K-308 K and sample temp. 273 K - 323 K)	<0.01K/K room temperature
Room temperature range	288 K - 308K
Weight	0.3 Kg
Case dimensions (lxbxh)	62 x 40 x 25 mm
Warm up time	30 minutes
Output voltage	approx. 42µV/°C (T type)

Figure 13.1. Connecting the BTO2000



Temperature instabilities 14

Symptoms of temperature instability 14.1

The most obvious way of detecting poor temperature regulation is by observing variations of the measured temperature on the Eurotherm display. With good regulation in the steady state the Eurotherm display should register a constant temperature or at most ± 0.1 K fluctuations. Such stability of course may not be possible if the experiment involves irradiating the sample with sufficient power such as during decoupling experiments.

Other obvious indications of poor regulation are

- Heater power display on front panel not steady
- Lock display not steady
- Air flow not steady

The effect of temperature instabilities may also be detected in spectra. Line broadening and chemical shifts are the most obvious effects, though 2-D artifacts may also be arise.

Troubleshooting 14.2

- Thermocouple too far away from bottom of sample tube : Check the position of the thermocouple tip.
- Leak in gas flow bath : Check the connection of the gas tube and the spherical coupling.
- Bad PID parameters of the temperature controller : Make a new self-tune of the controller.

BVT3000 Manual Operation

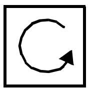
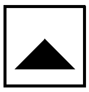
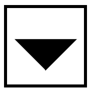
15

How to perform self-tuning manually 15.1

The purpose of the self-tuning procedure is to adapt the P.I.D parameters to suit the process loop conditions. Self-tuning should be initiated when an element of the process is changed, the probe for instance (see ***the Edte User manual***). For best results, the sample temperature should be stable when self-tuning is started.

When a self-tune is performed the following parameters are calculated : Pb, Ti, Td and possibly Cbl or Cbh.

Procedure :

- Switch off the heater at the front panel.
- Change the set point if required. Wait until the measured temperature has stabilized.
- Use the  button to scroll to St
- Press the  and  buttons simultaneously
- Switch on the regulation heater (11) at the front panel. Once self-tuning has started, the SP indicator will flash for 1 minute and an A-T indicator will appear on the upper right corner.
- After 1 minute, the S-T indicator will stop flashing and the A-T indicator will start flashing and continue to flash until the self-tune has finished.

Configuring the Eurotherm controller 902 15.2

Sensor selection 15.2.1

The BVT3000 can be used with different types of sensors :

- Thermocouple T (standard), E or K
- BTO2000
- PT100 sensor

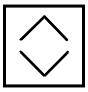
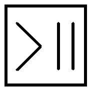
Warning: Never connect two types of sensors at the same time on the BVT3000.

The EUROTHERM 902 controller must be configured to work with the right type of sensor.

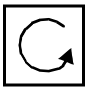
The configuration is done with the Eurotherm 902 controller keypad (or by software in the EDTE program).

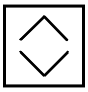
Proceed as follows:

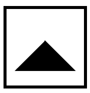
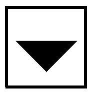
1. Switch off the main power.

2. Press the two left-most keys   simultaneously while turning the power on.

3. The message **CONF** and **UCONF** appears on the display.

4. Press the scroll button  until ICONF is displayed.

5. Press the left button  until C1 appears.

6. Now press the increment button :  or decrement button : 

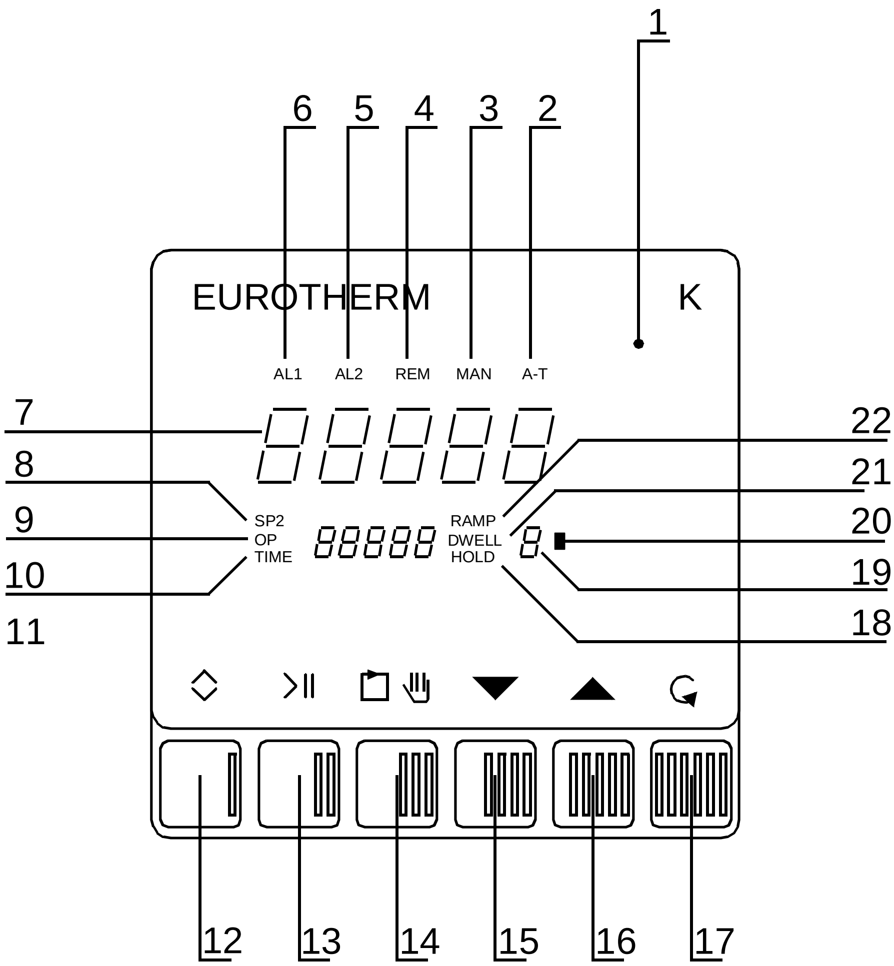
until the 4 digit code is displayed. This code must be changed to select the new sensor.

sensor	code C1
T thermocouple internal CJC	0004
K thermocouple internal CJC	0003
E thermocouple internal CJC	0012
Pt100	0024
BTO2000	1004

7. With the left selection button select the blinking digit to be modified and change the value with the increment or decrement button . When the code is correct press the scroll button. C2 will be displayed.

8. Press the selection button ,until **ICONF** appears. Press the scroll button until **LEAVE** appears. Press the left selection button again. The configuration is now complete and the temperature should now be displayed.

Figure 15.1. Eurotherm front panel (W4M110468)



1. Front panel
2. Illuminated when either self or adaptive tune is active
3. Illuminated when manual control is engaged
4. Illuminated when Remote Analogue Setpoint is enabled
5. Flashes when Alarm 2 is active
6. Flashes when Alarm 1 is active
7. Always indicates the Measured values except for the first 3 seconds after power up when the software version number is indicated
8. SP : Current of working Setpoint. SP2 : setpoint 2 value and selected
9. OP output power
10. TIME : Time remaining
11. Secondary display used to indicate all other functions of the instruments
12. Select (Turbo). The Select/Turbo or «I» key allows access to a scroll list for each option from the main scroll list. This key is also used in conjunction with the UP or DOWN key to accelerate the change of a parameter.
13. Run / Hold. The Run/Hold or «II» key is used exclusively to operate the program/ramp facility. If the program/ramp feature has been configured then ope-

rating this key the first time will cause the loaded program /ramp to run. Subsequent operations of this key will toggle the program/ramp condition from run to hold.

14. Auto / Man. The Auto/Manual or «III» key allows the controller to be toggled between the automatic and the manual condition.
15. Decrement. The Down or «IIII» key decrements the parameter appearing in the lower display.
16. Increment. The Up or «IIIII» key increments the parameter appearing in the lower display.
17. Scroll. The Scroll or «IIIIII» key is used to access individual parameters in a particular scroll list
18. Hold, DWell, Ramp + Time : Illuminated when a program or ramp is active, and indicates the current state of the function
19. See 18.
20. Flashes when an instrument transmits a message over the digital communications bus.
21. See 18
22. See 18

Eurotherm 847 configuration *15.3*

The EUROTHERM 847 controller must be configured to work with the right type of sensor.

To access the configuration mode, a switch located inside the 847 controller must be closed.

☞ ***The switch must be closed only during the configuration mode.***

Proceed as follows:

- Switch off the main power.
- Unscrew the EUROTHERM controller front plate.
- Remove the module out of its cabinet.

The switch **WB1** is located on the left side at the rear of the module.

- Close the switch.
- Insert the controller module and replace the front panel.
- Switch on the main power.

- Press the button [PAR] until «Sn» appears. («Sn» is the mnemonic for sensor). Then select the sensor type: press the up [▲] or down [▼] key until the correct sensor appears ***"Eurotherm 847 sensor selection" on page 84***.

Table 15.1. Eurotherm 847 sensor selection

sensor type	Sn
T thermocouple internal CJC	t tc
BTO2000	t tc
Pt100	rtd3

If the sensor is a thermocouple or a BTO2000 you must select also the type of (**C**old **J**unction **C**ompensation). Press the par **PAR** key until CJC appears and select with the up and down key. See (***"CJC selection" on page 84***)

Table 15.2. CJC selection

sensor type	Cjc
T thermocouple	int (internal)
BTO2000	0 °C (external at 0 °C)
Pt100	X (don’t care)

- When the configuration is finished, switch off the main power, remove the controller once again, and **open the switch.**

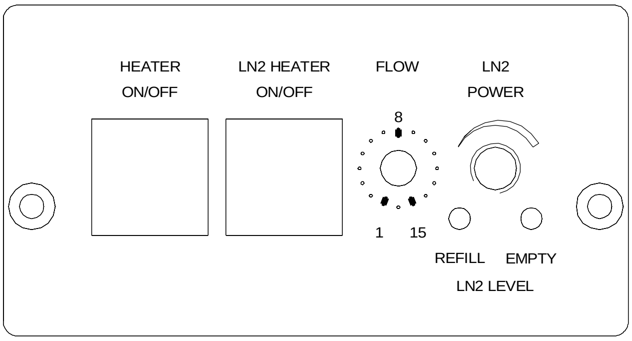
- Finally close the controller and switch on the power supply.

BMCM - Manual Control Module 15.4

For detailed informations, refer to ***the BMCM User manual***

The BMCM is an electronic module which allows to control manually the main functions of the temperature unit. It can be used with a BVT3000 or a BVT3300.

Figure 15.2. BMCM Front panel



The following functions of the temperature unit can be controlled :

- Probe Heater

The left push button of the module turns on the main probe heater. The heater status is indicated by a green led in the button.

- LN2 Heater

The right push button turns on the LN2 evaporator heater. The LN2 evaporator heater status is indicated by a green led in the button. The status of the LN2 level sensors are indicated by two red leds on the bottom. The LN2 heater power can be set with the rightmost potentiometer.

- Gas Flow Control

A knob permits to select manually stepwise a gas flow beetween 0 and 2000 l/h.

Table 15.3. Gas flow control

Knob position	Liter/hour
0	0
1	135
2	270
3	400
4	535
5	670
6	800
7	935
8	1070

Table 15.3. Gas flow control

Knob position	Liter/hour
9	1200
10	1335
11	1470
12	1600
13	1735
14	1870
15	2000

XWIN-NMR Software 16

XWIN-NMR configuration 16.1

In order for the Variable Temperature Unit (VTU) to be operated from the spectrometer keyboard it must first be linked to the spectrometer computer. The communication is achieved through an RS232 cable which connects the back panel of the VTU to the SIB board of the computer (see figure ***"Connecting Basic System" on page 14***). The software must know to which “tty “channel on the SIB board of the computer that the connection is made. When this has been done the unit is said to be “configured”.

- From within XWIN-NMR enter the command “cfte”
- You will be prompted with the question
- Which device is used for Temperature Unit tty—

    Simply enter two digits corresponding to the tty port e.g. 01,03 etc. and press return.

The VTU is now configured.

The channel is used to operate the VTU can be seen in the file

/u/conf/instr/<instrument name>/rs232_device/temp

Edte 16.2

For detailed informations, refer to ***the Edte user manual.***

Although the Eurotherm controller may be operated manually, it is far easier to use the Edte software.

Edte enables various parameters to be monitored or set using a user friendly graphical interface.

Performance plots 17

Plot 1 17.1

Room temperature and sample temperature correlation

Sample :

$K_3Co(CN)_6$, Potassium Hexacyanocobaltate.

Sample concentration /

1M

Sample temperature :

Mesured by observing frequency of ^{59}Co peak

Regulation :

BVT3000, BTO2000, BCU05

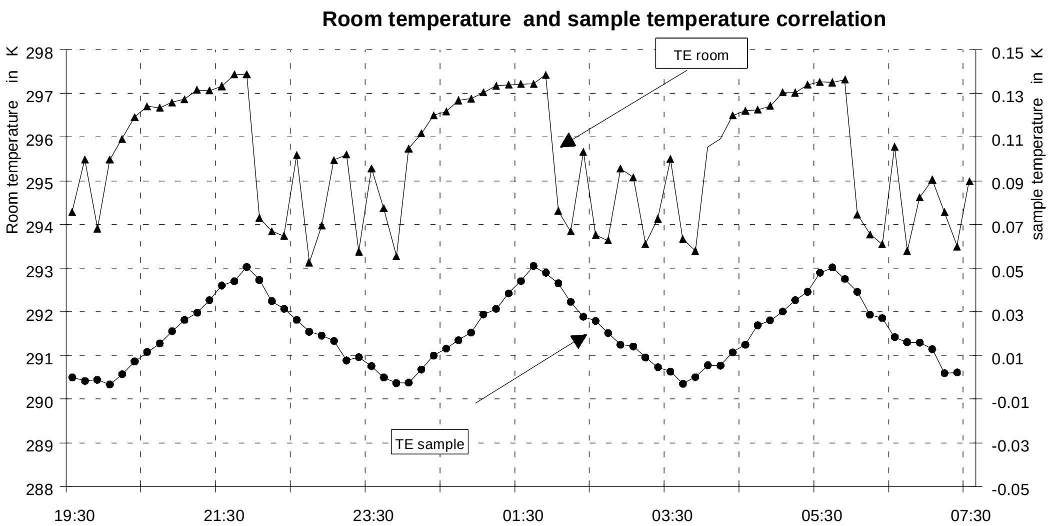
Conditions :

Large variations in room temperatures caused by switching room air conditioning on and off.

Conclusion :

Plot 1 displays the regulation ability of the temperature accessories under extreme conditions. A room temperature variation of almost 5 K has been reduced to 0.05 K sample temperature variation. This represents a sample variation of 0.01 K per degree room temperature variation.

Figure 17.1. Room and sample temperature correlation (plot 1)



Plot 2 17.2

Room and sample temperature correlation

Sample :

$K_3Co(CN)_6$, Potassium Hexacyanocobaltate

Sample temperature :

Measured by observing frequency of ^{59}Co peak

Regulation accessories :

BVT3000, BTO2000, BCU05

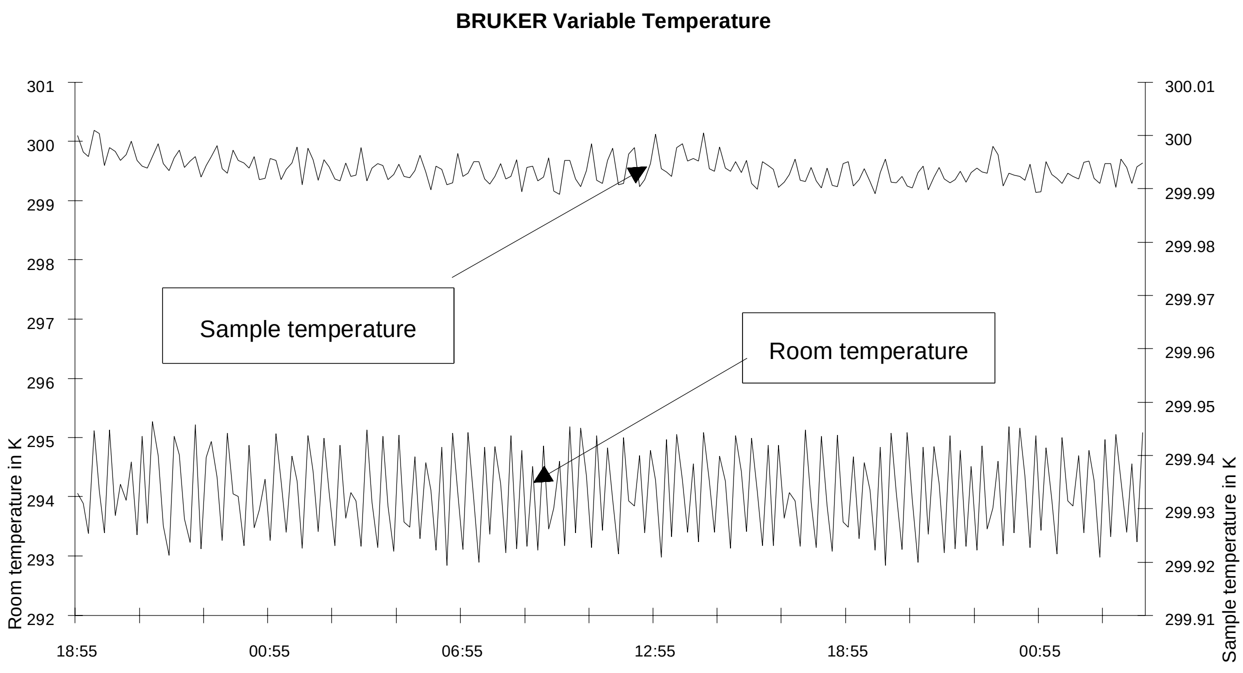
Conditions :

Typical variations in room temperatures.

Conclusion :

Plot 2 displays the regulation ability of the temperature accessories under typical conditions. A room temperature variation of ±1 K over a long period is fairly normal for a room with typical air conditioning. The plot shows that these room temperature variations result in sample temperature variations of less than 0.01 K. This represents a sample temperature variation of less than 0.01 K per degree room temperature variation.

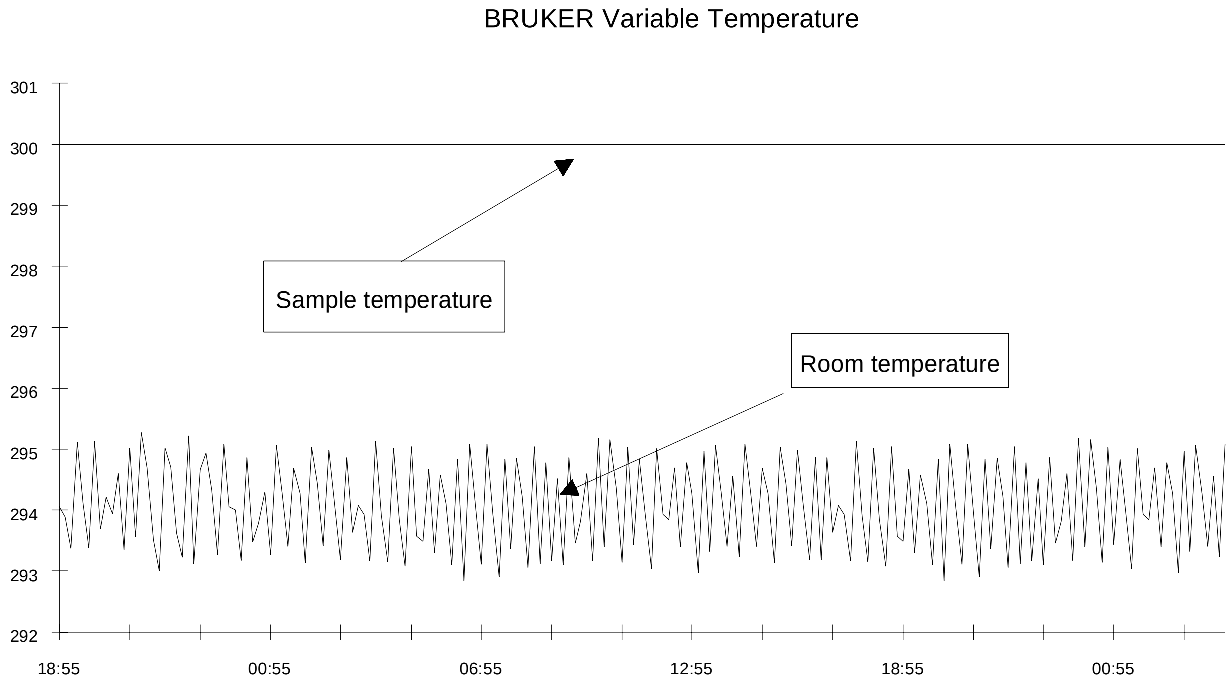
Figure 17.2. Room and sample temperature correlation (plot 2)



Plot 3 *17.3*

This is the same data except that room temperature and sample temperature have been plotted with the same scale.

Figure 17.3. Room temperature and temperature correlation (plot 3)



Plot 4 *17.4*

Cooling stability of BCU05

Sample :

$K_3Co(CN)_6$, Potassium Hexacyanocobaltate

Sample temperature :

Measured by observing frequency of ^{59}Co peak

Regulation : None

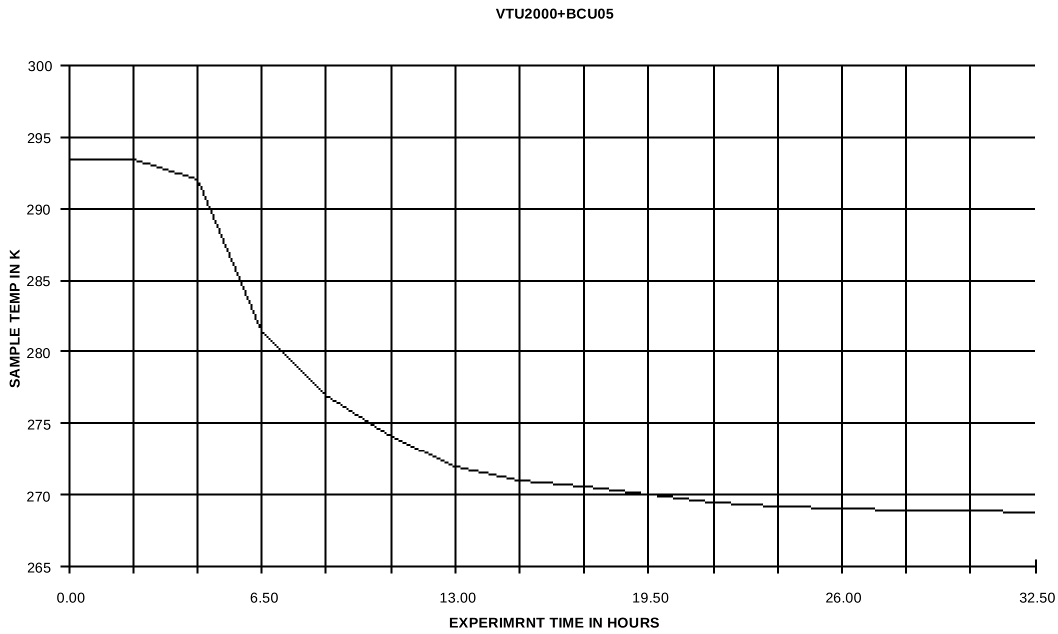
Conditions :

The BCU05 was switched on and the measurements started immediately.

Conclusion :

Plot 4 displays the fall in sample temperature with time after switching on the BCU05. It is clear that the cooling unit requires a start up time of only 30 minutes.

Figure 17.4. Cooling stability of BCU05



Plot 5,6 — 17.5

Noesy experiment on peptide

These two plots demonstrate the improvement in 2-D spectra as a result of optimum temperature regulation.

- Plot 5

  was acquired under conditions of poor temperature regulation with sample temperature variations of approximately 0.2 K.

- Plot 6

  This plot is the same experiment with the same sample only with optimum temperature regulation. A BVT3000 along with a BCU05 and BTO2000 were used to reduce temperature fluctuations to less than 0.1 K. The improvement in spectrum quality is clear.

Figures

Tables