ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

Temperature NMR

Advanced Operation Training Course

1. Hardware

Safety information: Spinner

POM

Kel-F

Ceramic

Spinner		**POM** (10 ~ 50°C)	
		Kel-F (-20 ~ 70 °C)	
	Ceramic (-150 ~ 150 °C)		

Safety information: Sample tube

Rate	Model	Thickness	Price (won)	MW	Temperature
< 600 MHz	WG-1000-7 High Throughput	0.43 mm	5,000	< 250	Only RT
for 400 MHz	WG-1228-7 Economy	0.43 mm	10,000	< 500	Only RT
for 600 MHz	WG-1241-7 Economy	0.43 mm	20,000	< 500	Only RT
for 400 MHz	527-PP-7 High precision	0.38 mm	30,000	500 <	< 120 ℃ (Max: 230 ℃)
for 600 MHz	535-PP-7 High precision	0.38 mm	40,000	500 <	< 120 ℃ (Max: 230 ℃)
	Quartz tube				< 120 ℃ (Max: 1300 ℃)

Low Temperature unit

BCU-I

BCU-II

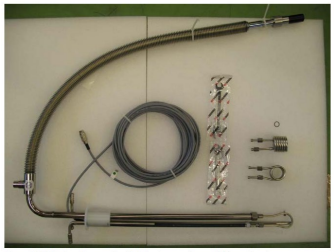


Figure 4.12 Heat exchanger kit with Johnston coupling and different inserts

LN2 Heat Exchanger

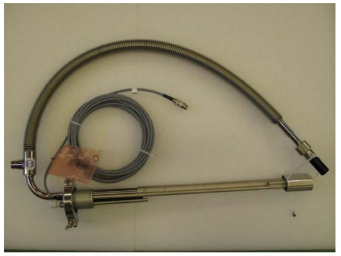


Figure 4.13 Evaporator Kit with Johnston coupling

LN2 Evaporator

<table>
<tr><td rowspan="4">Chiller</td><td colspan="3"></td><td>BCU-I
(0 ~ 25°C)</td></tr>
<tr><td colspan="2"></td><td>BCU-II
(-40 ~ 0 °C)</td><td></td></tr>
<tr><td></td><td>-100 °C ~
Unstable</td><td>LN2 Evaporator
(-80 ~ -40 °C)</td><td>~ 0 °C
Unstable range</td><td>Danger
(Burn out heater)</td></tr>
<tr><td colspan="2">LN2 Exchanger
(-150 ~ -40 °C)</td><td>~ 0 °C
Unstable range</td><td>Danger
(Burn out heater)</td></tr>
</table>

VT Flow for TEMP NMR

Temp. (°C)	-150 to -80	-80 to 0	0 to 80	80 to 120	80 to 150	150 to 180
VT gas (L/h)	1800 to 1200	1200 to 670	670 to 535	535 to 670		535 to 800
Recom. VT gas (L/h)	1200	1000	535			
Shim gas	20	20	0	0 to 20	20 to 30	40 to 60
Flush gas	5 to 10	5	0	5	5	5

Safety information: Materials

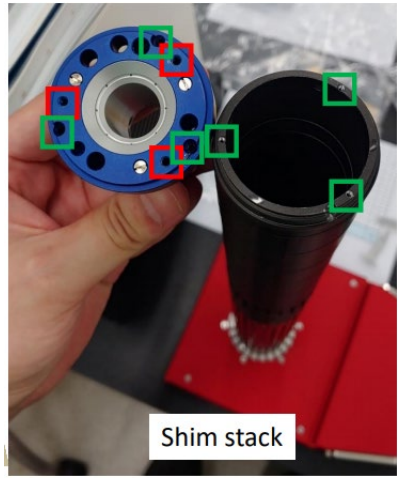
< Change rate of temperature >

Probe temperature control rate: 5°C/min

Target temperature stabilized time: 5 - 10 min

Shim system: -52°C < T < 80°C (221 K < T < 353 K), under 5 °C show error massage

Cryo system: 5°C < T < 80°C (278 K < T < 353 K)



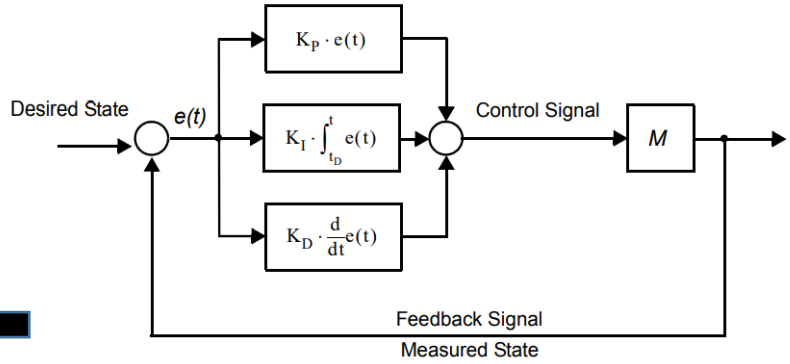
<Safety information: Materials>

1) Epoxy : T < +80 °C
2) Cu Coil layer: T > -52 °C
3) Magnet flange (O-Ring): 3°C < T < 80°C at long term experiments

2. Software

What is Self-Tune

Self-Tune
(Stabilized PID control system)



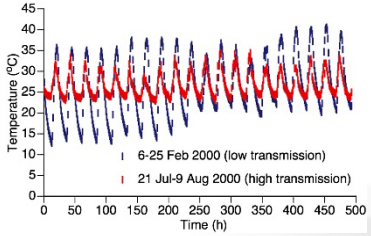
Ziegler–Nichols method

Tune the three parameter in PID

1) Control target temp
2) Gas flow
3) VT gas

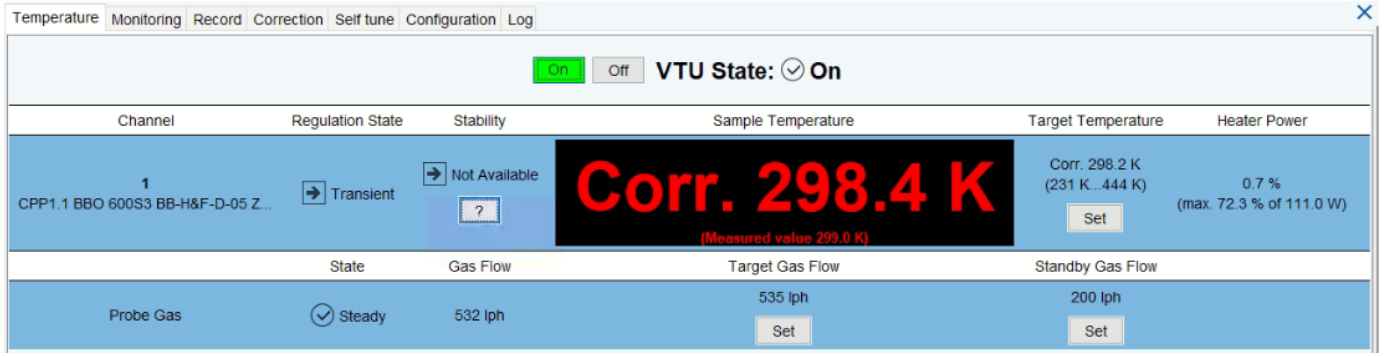
Three weighted terms
1) Proportional
2) Integral
3) Derivative

Stabilization of Temperature fluctuation

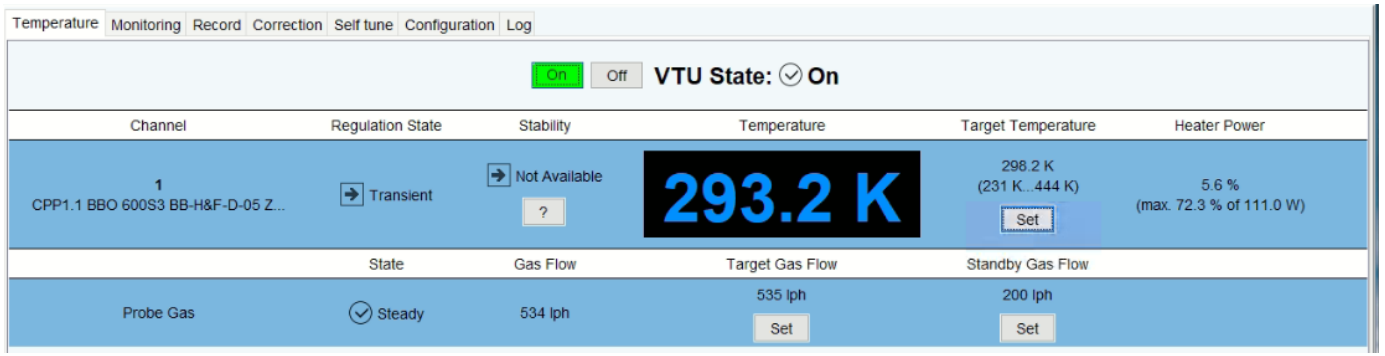


Sensor of Temperature

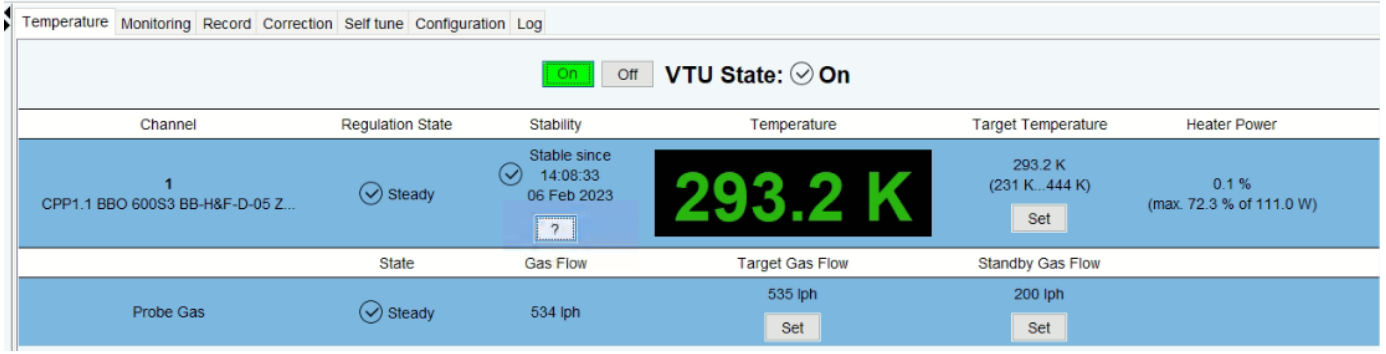
Red:
Change Temp



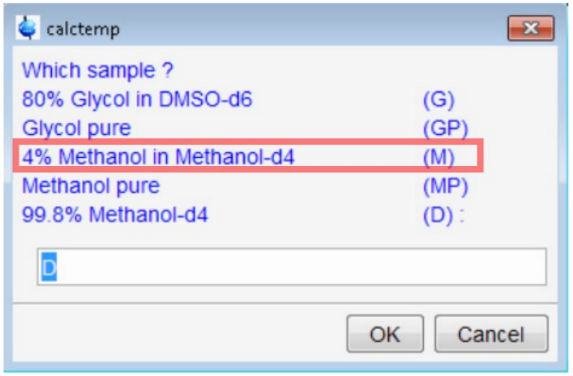
Green:
Reach target Temp



Blue:
Stabilized Temp



Temperature calibration



Command: ***calctemp***

1) 80 % Ethylene Glycol in DMSO-D6

Temperature	Equation
300K - 380K	$T = \frac{4.218 - \boldsymbol{\Delta\delta}}{0.009132}$

2) 100 % Ethylene Glycol

Temperature	Equation
300K - 380K	$T = \frac{4.637 - \boldsymbol{\Delta\delta}}{0.009967}$

$$\boldsymbol{\Delta\delta} = CH2 - OH \ \ chemical\ shift$$

3) 4% Methanol in Methanol-D4

Temperature	Equation
180K - 300K	$T = \frac{3.86 - \boldsymbol{\Delta\delta}}{0.00782}$
180K - 230K	$T = \frac{3.72 - \boldsymbol{\Delta\delta}}{0.007143}$
230K - 270K	$T = \frac{3.92 - \boldsymbol{\Delta\delta}}{0.008000}$
270K - 300K	$T = \frac{4.109 - \boldsymbol{\Delta\delta}}{0.008708}$

4) 100% Methanol

Temperature	Equation
180K - 300K	$T = -23.832\boldsymbol{\Delta\delta}$^2-29.46 $\boldsymbol{\Delta\delta}$+403
180K - 225K	$T = \frac{3.76 - \boldsymbol{\Delta\delta}}{0.007003}$
220K - 270K	$T = \frac{3.99 - \boldsymbol{\Delta\delta}}{0.008001}$
265K - 313K	$T = \frac{4.31 - \boldsymbol{\Delta\delta}}{0.009208}$

3. High Temperature

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Check list (High temperature)

1. Check Solvent (BP, Boiling Point)
2. Check Sample tube quality (527-PP or 535-PP, etc..)
3. Check spinner
   1) POM (10 ~ 50 °C)
   2) Kel-F (-20 ~ 70 °C)
   3) Ceramic (-150 ~ 150 °C)
4. Check (Related to Temperature range)
   1) Recommend VT gas flow
   2) Shim gas flow
   3) Flush gas flow
5. Check Shim coil temperature during experiment

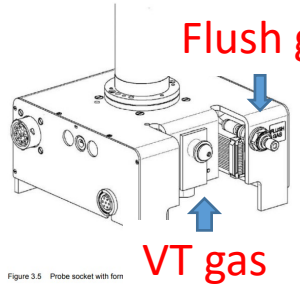

Figure 3.5 Probe socket with fom

<Safety information: Materials>
1) Epoxy : T < +80 °C
2) Cu Coil layer: T > -52 °C
3) Magnet flange (O-Ring): 3°C < T < 80°C at long term experiment

Shim system: -52°C < T < 80°C (221 K < T < 353 K), under 5 °C show error massage

Cryo system: 5°C < T < 80°C (278 K < T < 353 K)

Temp. (°C)	-150 to -80	-80 to 0	0 to 80	80 to 120	80 to 150	150 to 180
VT gas (L/h)	1800 to 1200	1200 to 670	670 to 535	535 to 670		535 to 800
Recom. VT gas (L/h)	1200	1000	535			
Shim gas	20	20	0	0 to 20	20 to 30	40 to 60
Flush gas	5 to 10	5	0	5	5	5

Procedure (High temperature)

1. Type *edte*
2. Set **Target gas flow** = 535 lph (l/p)
3. Click **Correction** Tab -> 보정된 Parameter값을 불러옴
   (없을 경우 Ethylene glycol을 이용하여 Calctemp로 correction value 생성)
4. Click **Self tune** (Wait 5 min)
   or Click **Restore to Channel 1** (Select an appropriate self-tune file)
5. Click **Temperature** Tab and click **Set on Target temperature**
6. Change **Shim gas flow ex) 0 to 80 °C = 0 lph, 80 to 120 °C = 20 lph, 120 to 150 °C = 30 lph**
7. Click **Monitoring** Tab (Check Current temperature, Target temperature)
8. Reach Target temp (Show green color), wait 10 min.
9. Progress Lock, Tune, Shim (This process is temperature dependence).
10. **Run Experiments**
11. Return to 25 °C (298 K)
12. Change **Shim gas flow = 0 lph** after reached 25 °C

Temp. (°C)	-150 to -80	-80 to 0	0 to 80	80 to 120	80 to 150	150 to 180
VT gas (L/h)	1800 to 1200	1200 to 670	670 to 535	535 to 670		535 to 800
Recom. VT gas (L/h)	1200	1000	535			
Shim gas	20	20	0	0 to 20	20 to 30	40 to 60
Flush gas	5 to 10	5	0	5	5	5

4. Low Temperature

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Check list (Low Temperature)

1. Check Solvent (MP, Melting Point)
2. Check Sample tube quality (527-PP or 535-PP, etc..)
3. Check spinner
   1) POM (**10 ~ 50 °C**)
   2) Kel-F (**-20 ~ 70 °C**)
   3) Ceramic (**-150 ~ 150 °C**)
4. Check (Related to Temperature range)
   1) Recommend VT gas flow
   2) Shim gas flow
   3) Flush gas flow
5. Check Shim coil temperature during experiment

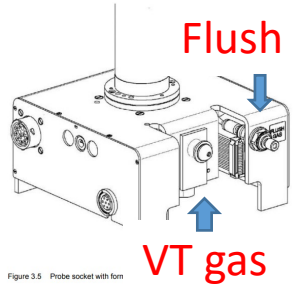


Figure 3.5 Probe socket with fom

<Safety information: Materials>
1) Epoxy : T < +80 °C
2) Cu Coil layer: T > -52 °C
3) Magnet flange (O-Ring): 3°C < T < 80°C at long term experiment

Shim system: -52°C < T < 80°C (221 K < T < 353 K), under 5 °C show error massage

Cryo system: 5°C < T < 80°C (278 K < T < 353 K)

Temp. (°C)	-150 to -80	-80 to 0	0 to 80	80 to 120	80 to 150	150 to 180
VT gas (L/h)	1800 to 1200	1200 to 670	670 to 535	535 to 670		535 to 800
Recom. VT gas (L/h)	1200	1000	535			
Shim gas	20	20	0	0 to 20	20 to 30	40 to 60
Flush gas	5 to 10	5	0	5	5	5

Procedure (Low Temperature)

1. Type *edte*
2. Set **Target gas flow** = 1000 lph (l/p)
3. Click **Correction** Tab -> 보정된 Parameter값을 불러옴
   (없을 경우 Methanol or 4% MeOD를 이용하여 Calctemp로 correction value 생성)
4. Click **Self tune** (Wait 5 min)
   or Click **Restore to Channel 1** (Select an appropriate self-tune file)
5. Click **Temperature** Tab and click **Set on Target temperature**
6. Change **Shim gas flow ex) -150 to 0 °C = 20 lph**
7. Click **Monitoring** Tab (Check Current temperature, Target temperature)
8. Reach Target temp (Show green color), wait 10 min.
9. Progress Lock, Tune, Shim (This process is temperature dependence).
10. **Run Experiments**
11. Return to 25 °C (298 K)
12. Change **Shim gas flow = 0 lph** after reached 25 °C

* If you want to change sample on Low temp condition, you must cool your sample!
(Room temp sample could make heat shock)

Temp. (°C)	-150 to -80	-80 to 0	0 to 80	80 to 120	80 to 150	150 to 180
VT gas (L/h)	1800 to 1200	1200 to 670	670 to 535	535 to 670		535 to 800
Recom. VT gas (L/h)	1200	1000	535			
Shim gas	20	20	0	0 to 20	20 to 30	40 to 60
Flush gas	5 to 10	5	0	5	5	5

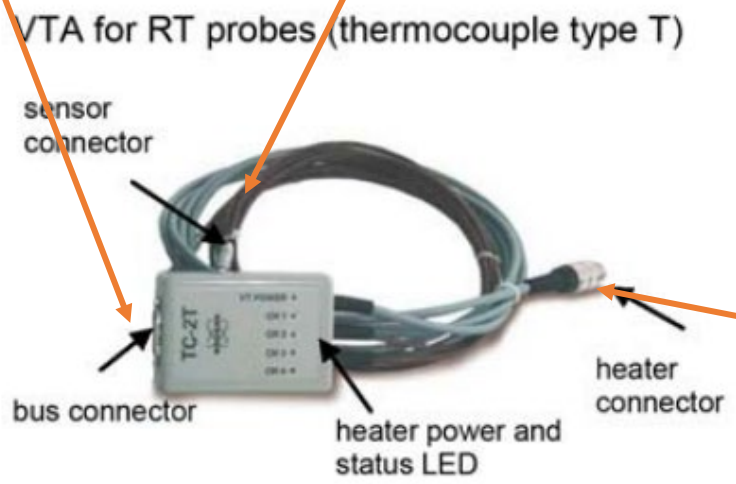
4. Control LT unit

LN2 Evaporator

Console

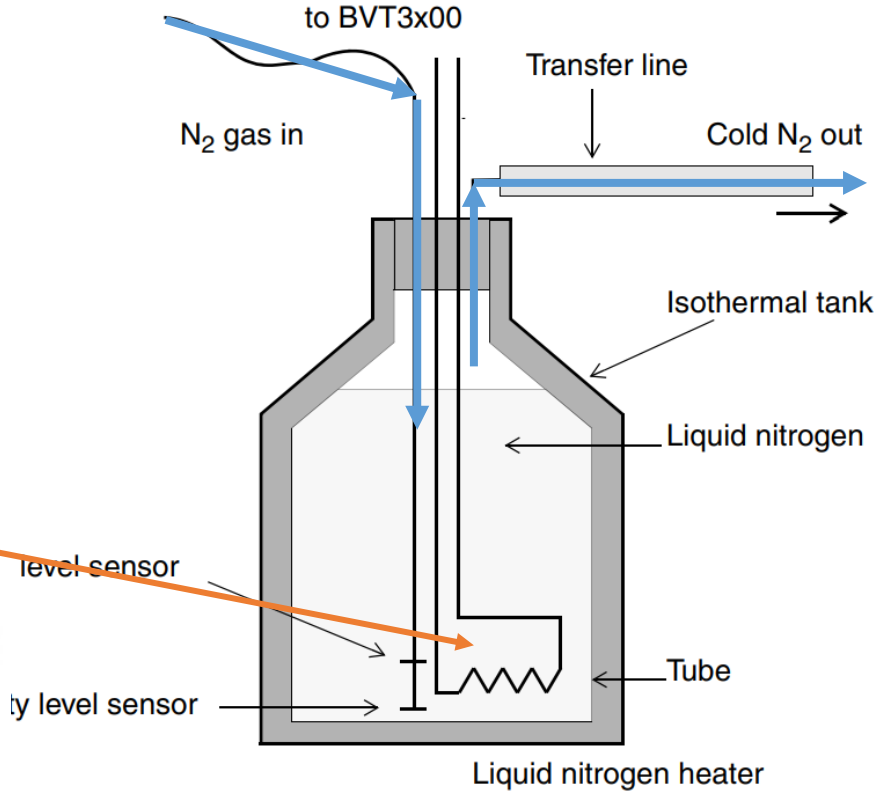
Probe

Directly use cool N2 gas
(Boiling LN2)



TC-2T

Figure 2.4. Evaporator principle



Procedure (Low temperature)

1. LN2 dewar에 LN2 충진
2. LN2 evaporator connector 와 TC-2T connector 연결
3. LN2 dewar에 heat exchanger를 천천히 넣은 뒤 Clamp로 잠금 (LN2 넘침 주의, 약 10시간 가동가능)
4. Probe의 기존 VT gas line(RT) 제거
5. Heat exchanger의 VT gas line(LT)와 Probe연결
6. 1) Type edte,
   2) Turn on HEATER and COOLING.
   3) Set 15 °C, flow rate = 535 L/h, set max of heater = 10 % (50% 이하 유지)
   4) Self tune 클릭 (or 기존 값 restore)
   5) 5 °C/min 의 속도로 온도조절이 되는지 확인
   6) Nitrogen boil off heater(=Cooling power) on cooling window의 CHANGE 클릭하여 조절
      > 너무 기화량이 높으면 Sample이 밀려올라감
7. 온도조절 완료 후 10분 대기 or Lock, tune, shim 수행
8. 실험 중 Shim coil 온도 체크 및 Shim flow 조절 (5 °C이하로 떨어지면 경고 메시지 발생)
   Shim system: -52°C < T < 80°C (-325 K < T < +353 K)
9. 실험종료 후 5 °C/min 의 속도로 온도로 25 °C로 조절
10. Sample heater와 Nitrogen boil-off heater 끄기
11. Heat exchanger의 VT gas line(LT)와 Probe 분리
12. VT gas line (RT) 연결

*** Sample 냉각 후 Magnet insertion (Sample의 온도가 너무 높으면 열충격에 의해서 Heater에 손상이 발생할 수 있음)

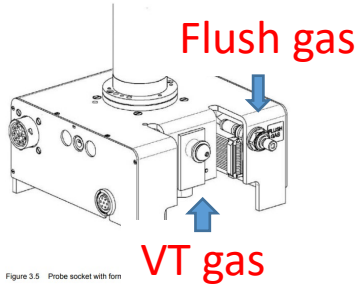


Figure 3.5 Probe socket with fom

http://www.uwyo.edu/chemistry/instrumentation/NMR/NMR-Useful%20Tips.html

LN2 Exchanger

Console

Probe

Indirectly use cooled N2 gas
(Exchange temperature)

VTA for RT probes (thermocouple type T)

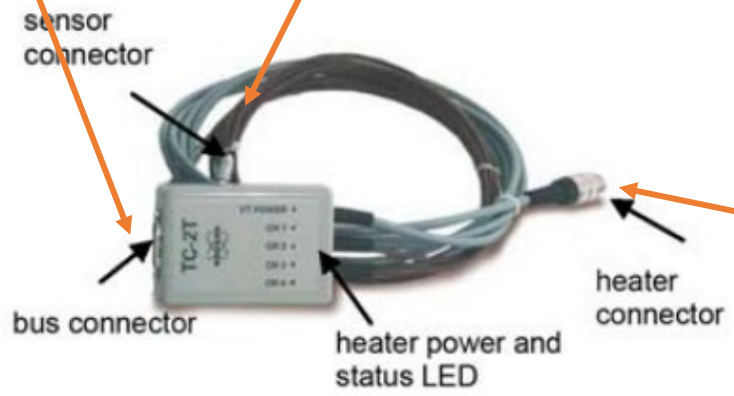
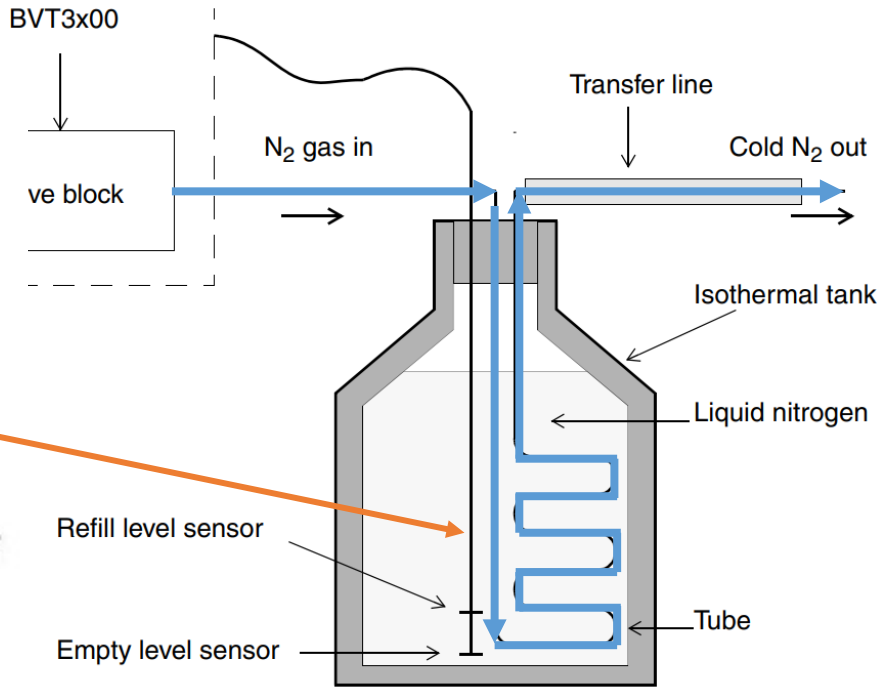
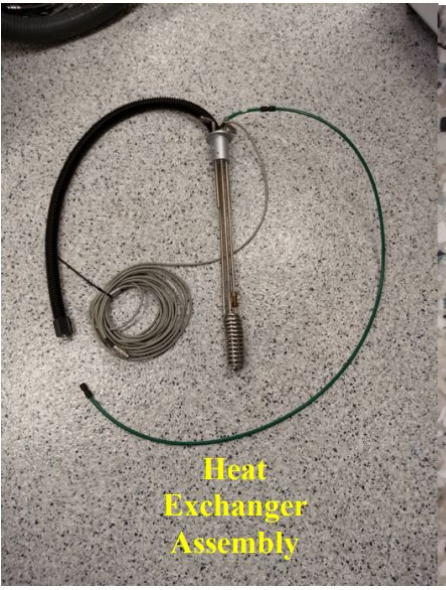
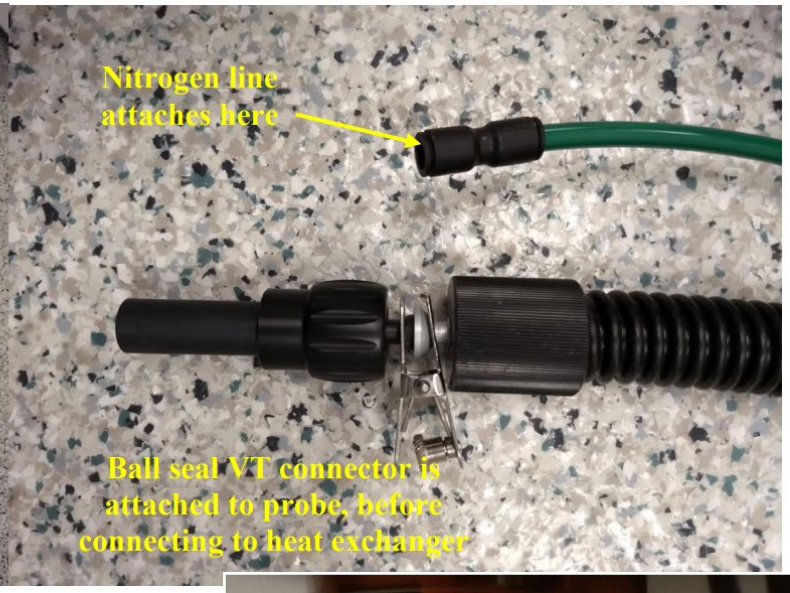


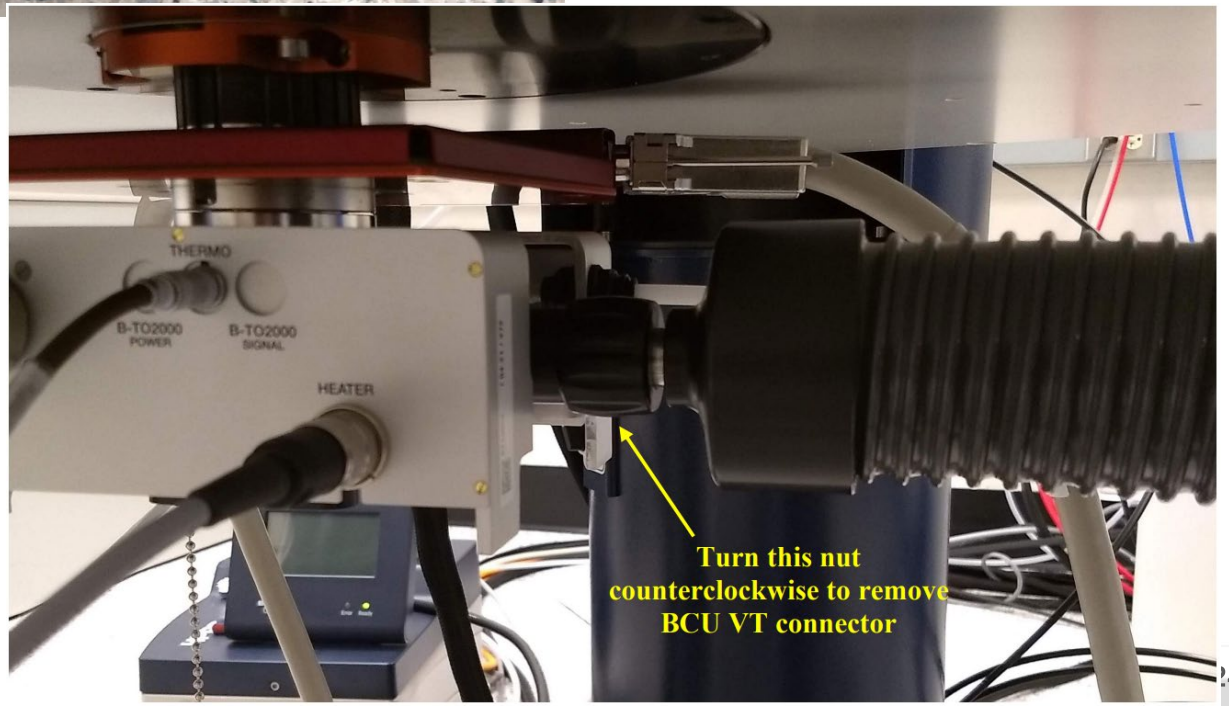
Figure 2.3. Exchanger principle





Heat Exchanger Assembly






VT GAS IN
MAX 6 BAR

Low Temperature unit

VTA for RT probes (thermocouple type T)

VTA for CryoProbe

Figure 4.16 Examples of VTA

Boiling liquid nitrogen -> Cold L-N2 gas

Working temp.: -40 ~ -150 ˚C

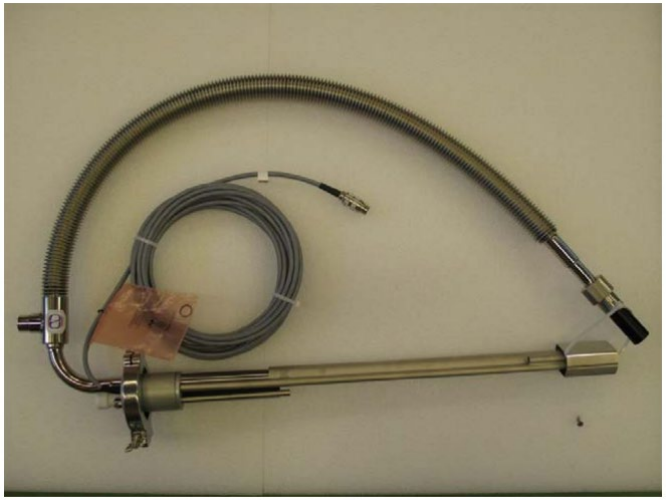


Figure 4.13 Evaporator Kit with Johnston coupling

Spinner

POM spinner

Range: 100 MHz to 400 MHz
Temp: +10 °C to + 50 °C

Kel-F spinner

Range: 500 MHz to up
Temp: -20°C to + 70 °C

POM spinner (500 MHz+)

Range: 500 MHz to up
Temp: +10 °C to + 50 °C

Ceramic spinner

Range: 500 MHz to up
Temp: -150 °C to +150 °C