ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

Diffusion Ordered SpectroscopY

Advanced Operation Training Course

1. DOSY of Theory

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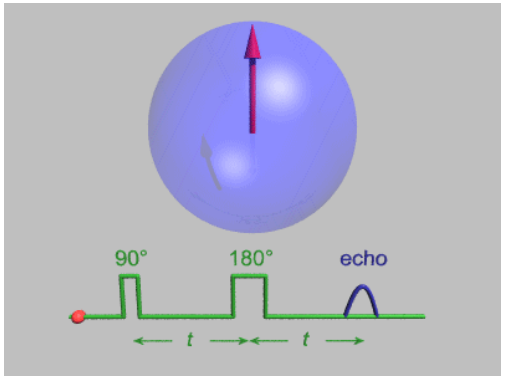
Spin echo (Hahn-echo) vs Gradient echo

SE (Spin Echo)

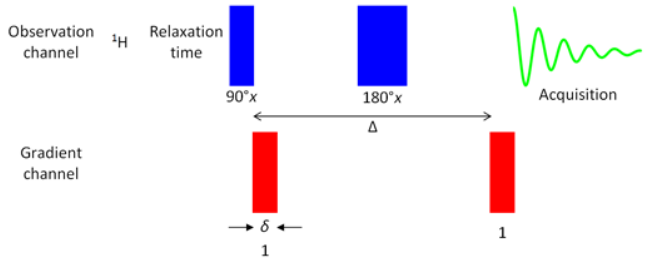


- Dephasing/Refocusing : Related T2
- Experiment time: Long

T2 time을 따라 dephasing이 일어나므로 실험시간이 길어짐

Origin pulse sequence of DOSY

PGSE (Pulsed Gradient Spin Echo)



- Dephasing/Refocusing : Use Gradient
- Experiment time: Middle
- Limited Diffusion Delay (T2*)

T2* = T2 in rotating frame

Gradient를 이용하여 강제로 Dephasing / Refocusing을 진행하므로 실험시간이 짧음, 대신 T2*시간이내로 Diffusion delay가 제한됨

STE (STimulated Echo)

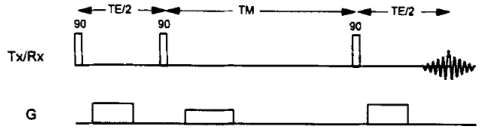


Figure 3 Pulse sequence used to generate a stimulated echo.

- Dephasing/Refocusing : Use Gradient
- Experiment time: Short
- Limited Diffusion Delay (T1)

3개의 90도 펄스와 Gradient를 이용하여 T2보다 상대적으로 긴 T1 을 Diffusion delay로 사용

https://magritek.com/2016/07/18/gradients-in-nmr-spectroscopy-part-5-the-pulsed-gradient-spin-echo-pgse-experiment/

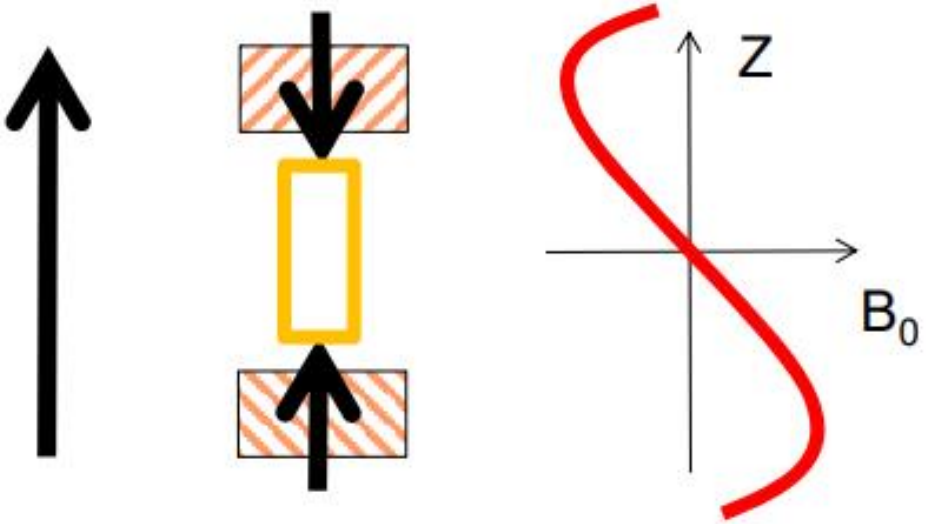
https://onlinelibrary.wiley.com/doi/epdf/10.1002/%28SICI%291099-0534%281996%298%3A4%3C269%3A%3AAID-CMR3%3E3.0.CO%3B2-X

Pulsed Field Gradients (PFG)

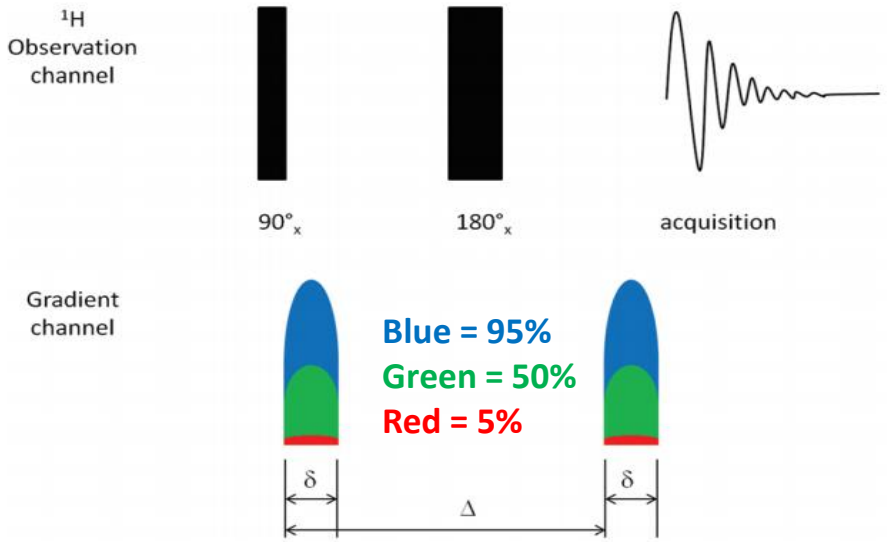
What is Gradient?

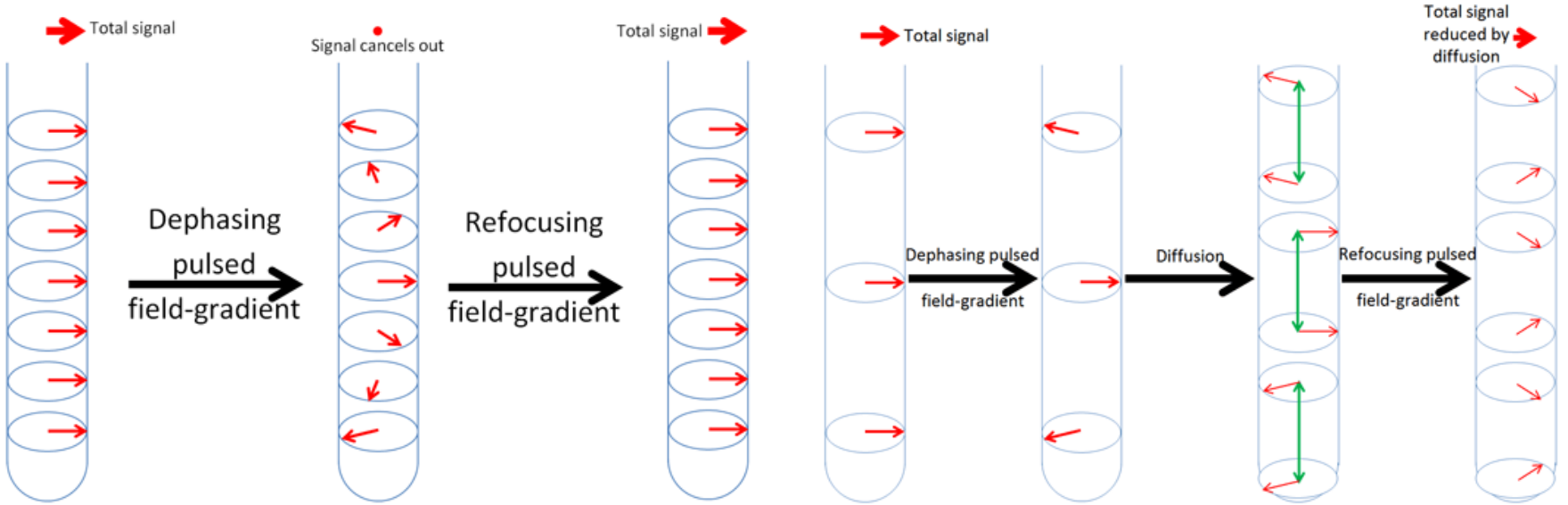
Use Gradient coil -> Make field gradient
-> Force Dephasing / Refocusing for Nuclear spin
-> Save time, Correct good data

Gradient coil을 이용하여 Magnetic field gradient 형성할 수 있음, 이를 이용 강제적으로 Nuclear spin의 Dephasing / Refocusing을 할 수 있음 -> 실험시간 단축, 정확한 데이터 획득 가능

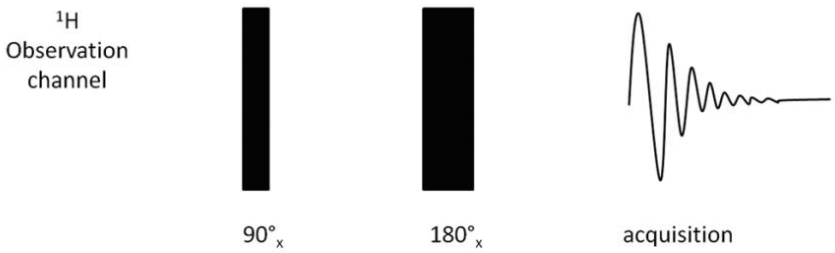


Pulsed field gradient spin-echo, PGSE



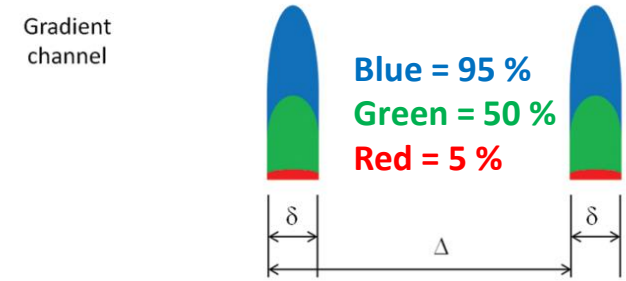


Gradient power vs I value

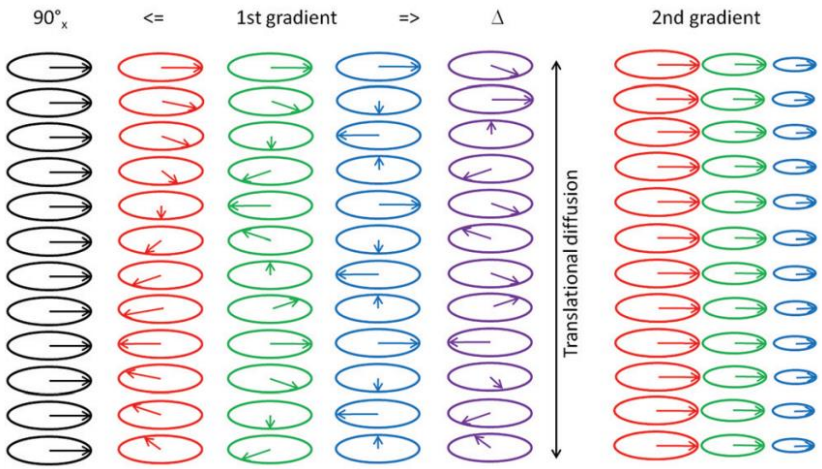


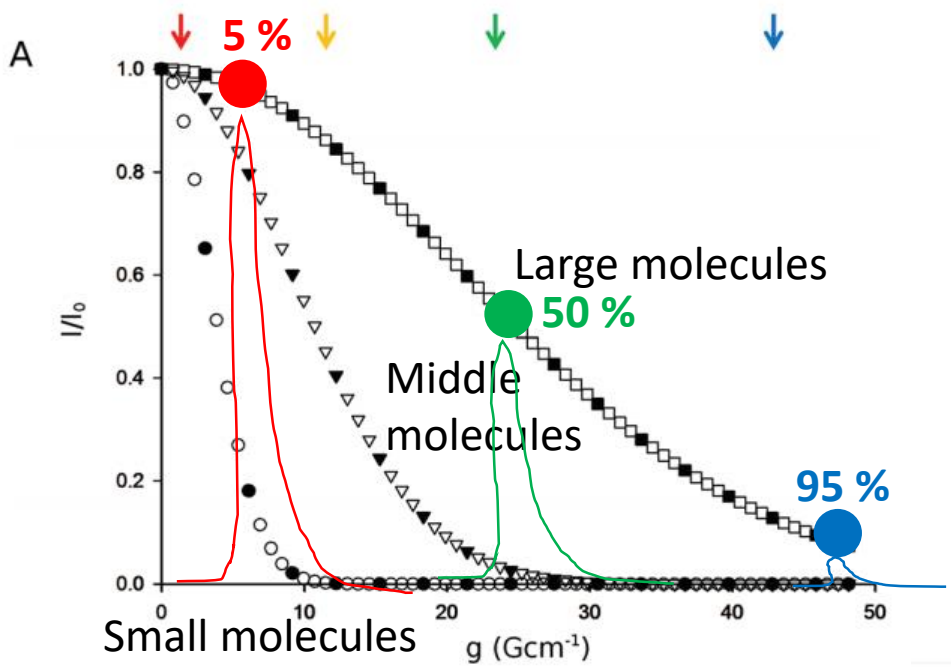
Δ diffusion time
δ gradient pulse length

Gradient induce dephasing (like grab)
Powerful grab makes small signal.



Small molecules = Diffuse quickly = Rapidly recovered magnetization
Large molecules = Diffuse slowly = Slowly recovered magnetization





https://pubs.rsc.org/en/content/articlelanding/2017/py/c7py01577a#!divAbstract

Equation

$$I / I_0 = e^{(-Dg^2\delta^2\sigma^2 g^2 \Delta')}$$

I -> Measure DOSY 2D
I0 -> Measure DOSY 2D
D20 -> Calibrate DOSY 1D
P30 -> Calibrate DOSY 1D

D diffusion coefficient (m^2 s^{-1}) Calculation value

g gyro-magnetic ratios of the studied nuclei

σ gradient shape factor

δ gradient pulse lengths Little Delta, **P30**

Δ diffusion time

Δ' diffusion delay Big Delta, **D20**

Peak Intensity (or integration) of 95% Gradient power I

Peak Intensity (or integration) of 5% Gradient power I_0

2. DOSY
Pulse sequence

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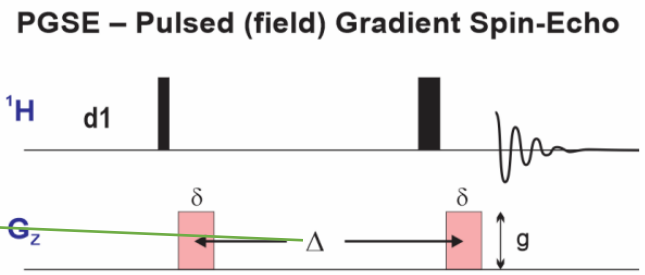
Stimulated Echo (STE)

PGSE (Pulsed field Gradient Spin-Echo)

Disadvantage

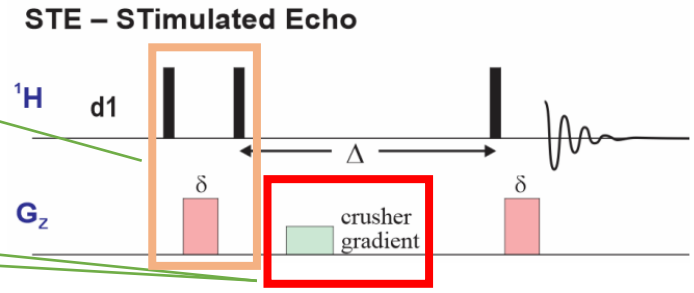
1. Poor sensitivity
   = Related transverse magnetization(T2*)
   (D20<T2)*
2. Chemical shift and J coupling dependence
   (180 pulse isn`t perfect for sample by sample)



STE (STimulated Echo)

Advantage

1. Remove transverse magnetization(T2) and
   Only Store longitudinally magnetization(T1)
   (D20<T1) [T2 ≤ T1]
2. Eliminate a lot of artifact
3. Reduce chemical shift and J coupling dependence



(Homo) Spoil gradient
(Crusher gradient)

Disadvantage

1. Eddy current

https://www2.chem.wisc.edu/~cic/nmr/Guides/Bavug/DOSY-cc_Bruk.pdf

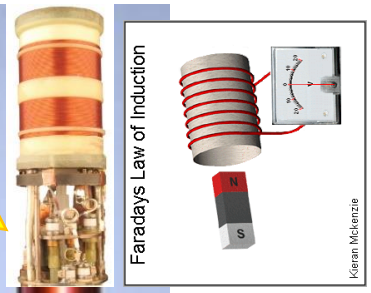
Eddy current

Gradient Coil

DOSY Experiment

USE

Field Gradient



Interaction

Interaction

Side effects

Side effects

Eddy current

Interaction of Metal & Field Gradient

Metal
of the magnet

Metal
of the probe

Longitudinal Eddy current Delay (LED)

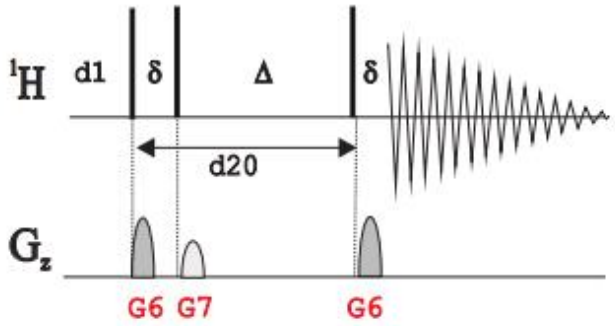
LED (**L**ongitudinal **E**ddy current **D**elay)
D21 = 5 ms (typically)
Eddy current = some ms to tens of ms

Advantage

1. Reduce **eddy-currents**
2. Reduce Disturbance of field-frequency **Lock**

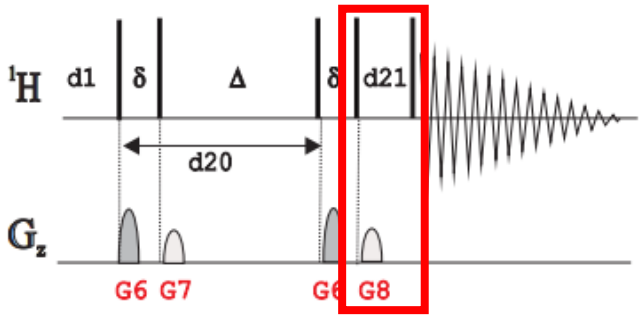
stegp1s

stegp1s1d



ledgp2s

ledgp2s1d



LED

Bipolar Pulse Pair (BPP)

BP (BiPolar)

Advantage

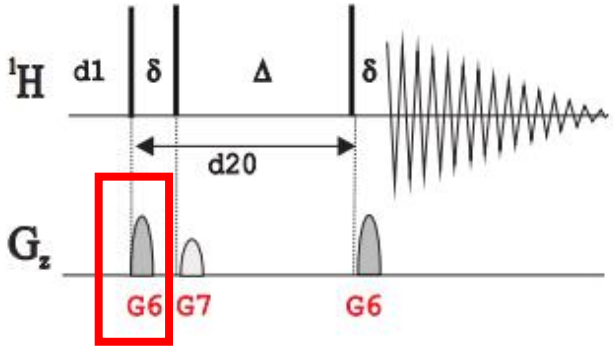
1. Reduce **eddy-currents** (95%)
2. Reduce Gradient imperfections
3. Reduce Disturbance of field-frequency **Lock**

Disadvantage

1. Phase Cycling
   (Minimum NS=8 / Preferably NS=16)

stegp1s

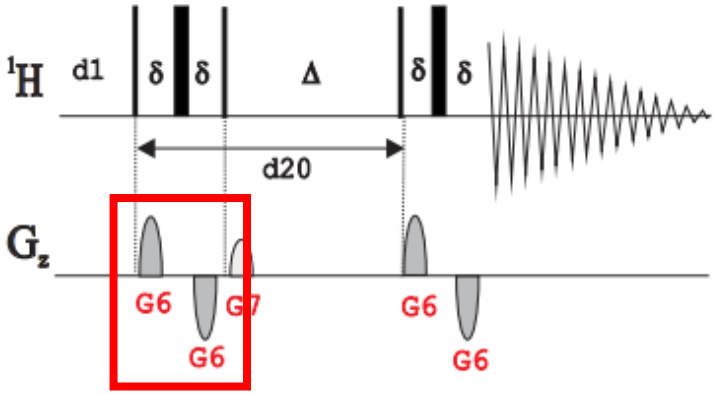
stegp1s1d



MP(Mono Polar)

stebpgp1s

stebpgp1s1d



BP(BiPolar)

https://www2.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/AV3_DOSY-diffusion.pdf

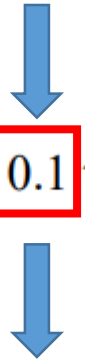
Diff (kappa)

Diff (kappa in VNMR)

1. Unbalancing of the bipolar pair reduces reliance on EXORCYCLE phase cycling
2. Diff = 0.2 (typically)

EXORCYCLE: Remove the effects of an imperfect refocusing pulse
(Phase cycling: at least NS = 8)

gpz1 = –gpz3 = 1, 20, 37, 49, 58, 66, 73, 80

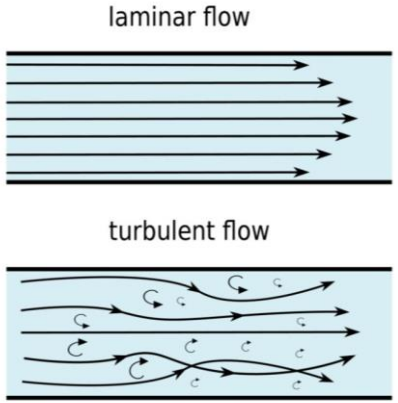


diff = 0.1 to 0.2

gpz1 = 1.1, 22, 40.7, 53.9, 63.8, 72.6, 80.3, 88
gpz3 = –0.9, –18, –33.3, –44.1, –52.2, –59.4, –65.1, –72

https://slidetodoc.com/coherence-selection-phase-cycling-and-gradient-pulses-purpose/

Convection compensation (CC)



DSTE (Double STimulated Echo)

-> CC(Convection compensation)

- Canceling all constant-velocity effect (laminar flow only)
- Convection cause
  1) Temperature gradients
  2) RF pulse heating effect
  3) Cryo-probe occur convection on room temp

Disadvantage

1. Reduce 50% of the magnetization is lost compared to the non-cc version

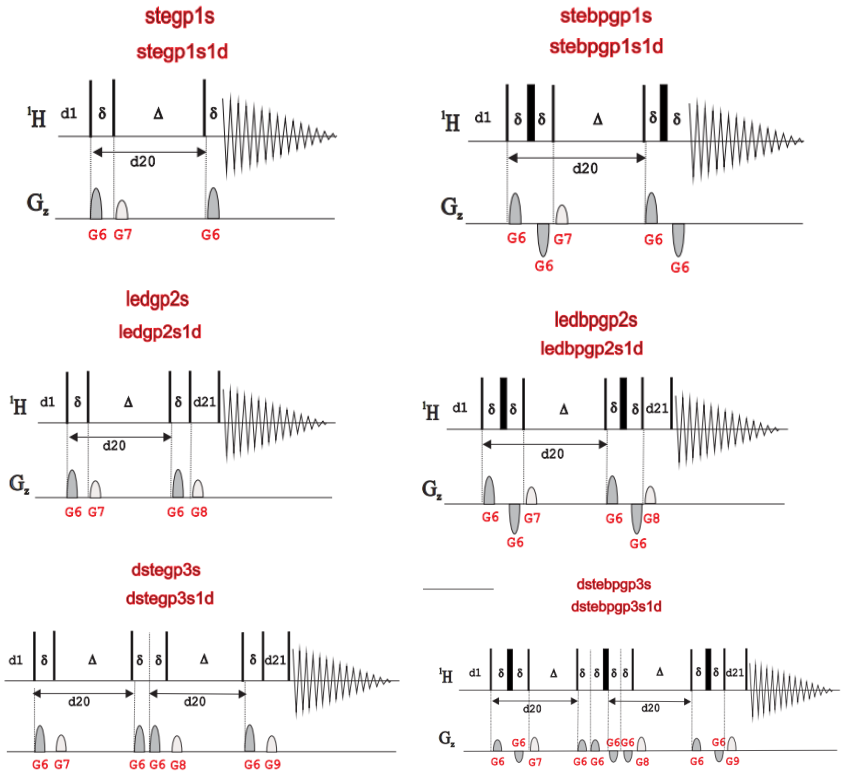
Minimize convection

1. Use 3 mm sample tube
2. Disconnect all air flow into the probe sample area
3. Turn off temperature regulation
4. Use a shorter sample with less volume.

https://www2.chem.wisc.edu/~cic/nmr/Guides/Bavug/DOSY-cc_Bruk.pdf

Stimulated Echo pulse, STE / LED

stegp1s = STE
stebpgp1s = STE + BP
stebpgp1s19 = STE + 3-9-19 watergate
ledbpgp2s = LED
ledbpgppr2d = LED + preset
dstebgp3s = STE + CC
dstebpgp3s = STE + BP + CC



Pulsed field **G**radient **S**pin-**E**cho (PGSE)
STimulated-**E**cho pulse (STE)
Longitudinal **E**ddy current **D**elay (LED)
Double **ST**imulated-**E**cho (DSTE)
BiPolar gradient (BP)

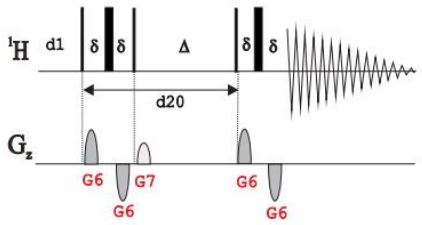
Origin of DOSY sequence
Minimization of the short T2 effects
Minimization of eddy currents
Convection **C**ompensation (CC)
Reduce eddy-currents (95%)
& Inhomogeneous background gradient

DOSY sequence in Varian

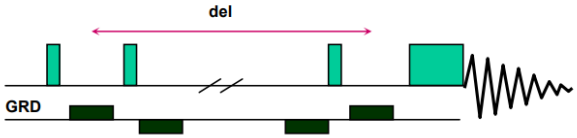
4.2.1 Dbppste (DOSY Bipolar Pulse Pair STimulated Echo) Experiment

Reference: Wu, D.; Chen, A.; Johnson, C.S., Jr., J. Magn. Reson. 1995, 115, Series(A), 260-264.

stebpgp1s
stebpgp1s1d



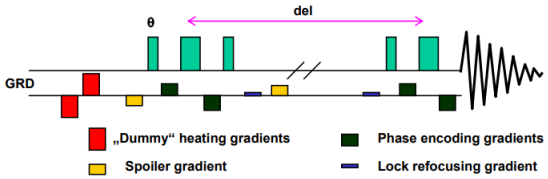
4.2.2 DgcsteSL (DOSY Gradient Compensated Stimulated Echo with Spin Lock) Experiment



Reference: Pelta, M.D.; Barjat, H.; Morris, G.A.; Davis, A.L., Hammond, S.J. Magn. Reson. Chem. 1998, 36, 706.

SL(Spin Lock):
Keep magnetization in the transverse plane

4.2.3 The "Doneshot" Experiment



Reference: M. D. Pelta, G. A. Morris, M. J. Tschedroff and S. J. Hammond: MRC 40, 147-152 (2002)
For eliminating radiation damping: M. A. Conell, A. L. Davis, A. M. Kenwright and G. A. Morris: Anal. Bioanal. Chem. 378, 1568-1573, (2004).

Oneshot DOSY: Possible NS=1 (Non phase cycling)

CC(Convection compensation) in Varian

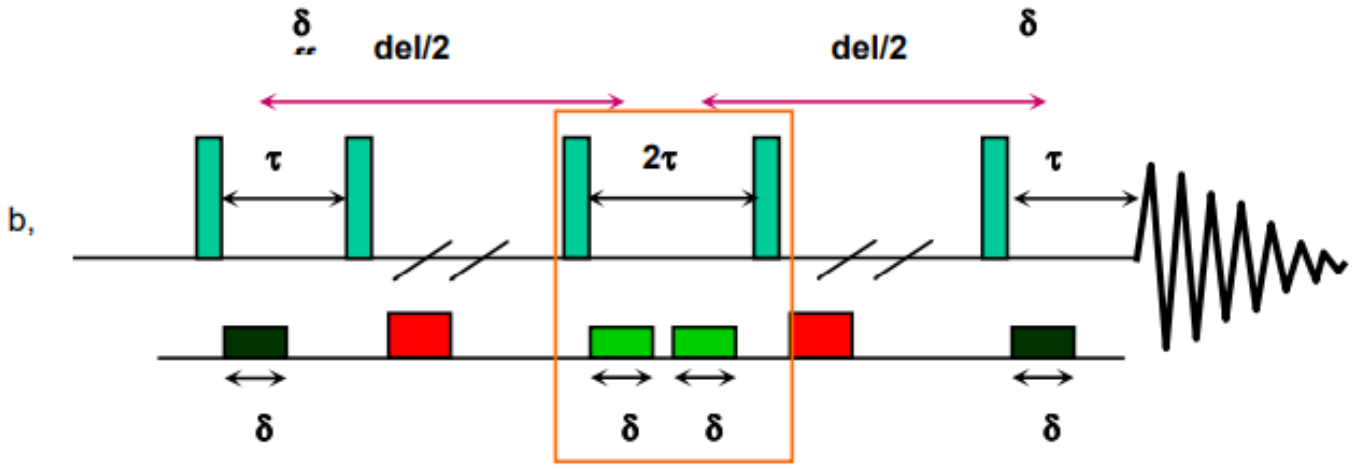
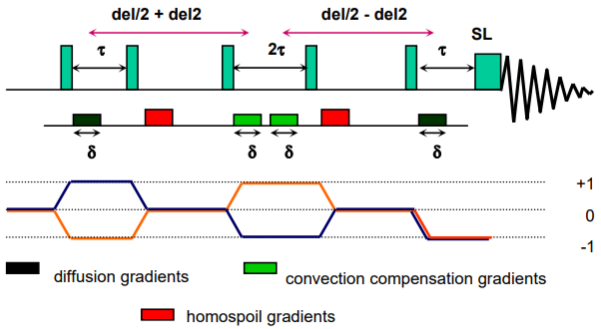


Figure 10 Modification of a gradient stimulated echo experiment with convection compensation.

DgsteSL_cc (Gradient STimulated Echo with Spin-Lock and Convection Compensation)
DgcsteSL_cc (Gradient Compensated STimulated Echo with Spin-Lock and Convection Compensation)
Dbppste_cc (Bipolar Pulse Pair STimulated Echo with Convection Compensation)
Dpfgdste (Pulse Field Gradient Double STimulated Echo)

CC(Convection compensation) in Varian

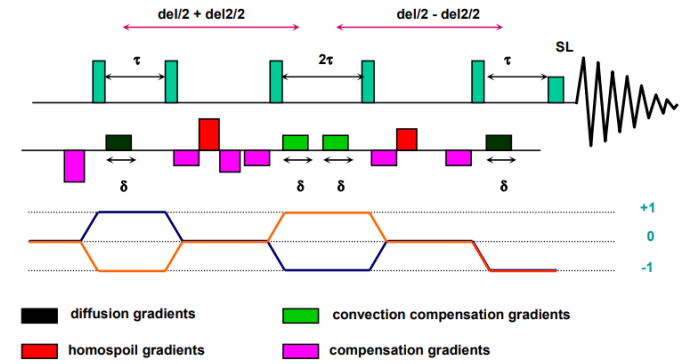
4.4.1.2. DgsteSL_cc (Gradient STimulated Echo with Spin-Lock and Convection Compensation)



Reference: A. Jerchow and N. Müller, J. Magn. Reson. 125, 372-375 (1997).

SL(Spin Lock): O
Gradient compensation: O
Convection compensation: O
Z-filter(LED): X

4.4.1.3 DgcsteSL_cc (Gradient Compensated STimulated Echo with Spin-Lock and Convection Compensation)



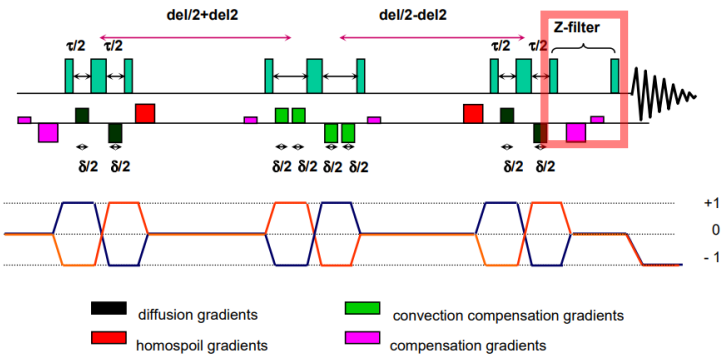
Reference: A. Jerchow and N. Müller, J. Magn. Reson. 125, 372-375 (1997).

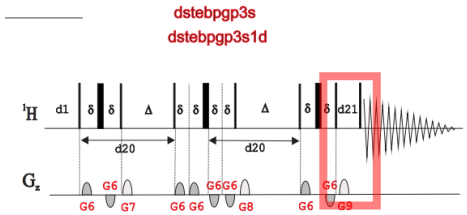
SL(Spin Lock): O
Gradient compensation: O
Convection compensation: O
Z-filter(LED): X

CC(Convection compensation) in Varian

4.4.1 Pulse Sequences with Convection Compensation

4.4.1.1. Dbppste_cc (Bipolar Pulse Pair STimulated Echo with Convection Compensation)

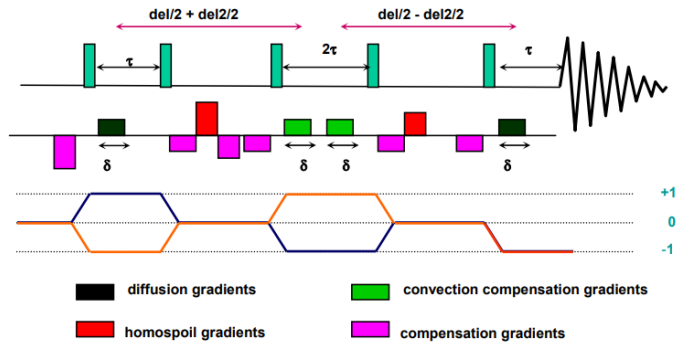




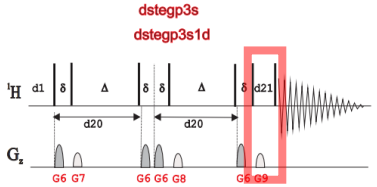
Z-filter(LED)

SL(Spin Lock): X
Gradient compensation: O
Convection compensation: O
Z-filter(LED): O

4.4.1.4. Dpfgdste (Pulsed Field Gradient Double STimulated Echo)



Reference: Nilsson M, Gil AM, Delgadillo I, Morris GA. Anal Chem 2004.76:5418-5422



Z-filter(LED)

SL(Spin Lock): X
Gradient compensation: O
Convection compensation: O
Z-filter(LED): X

One-shot DOSY

MAGNETIC RESONANCE IN CHEMISTRY
Magn. Reson. Chem. 2002; **40**: S147–S152
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/mrc.1107

MRC

A one-shot sequence for high-resolution diffusion-ordered spectroscopy

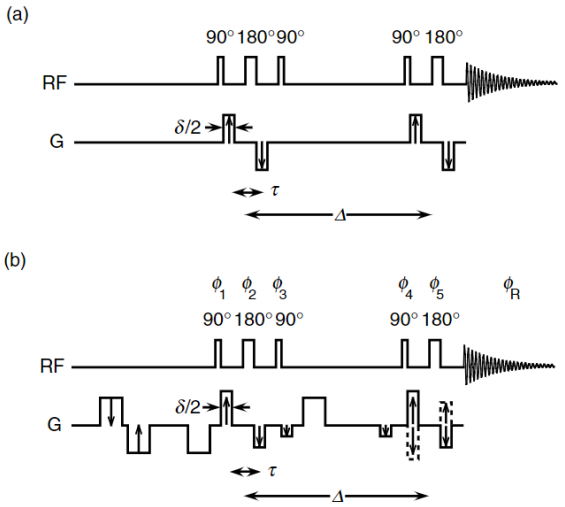
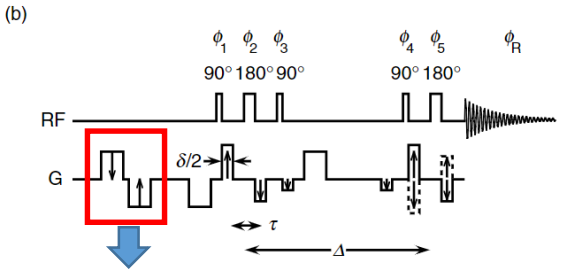


Figure 1. Radiofrequency (RF) and gradient (G) pulse sequences for DOSY. (a) Bipolar pulse pair stimulated echo (BPPSTE) sequence; (b) the proposed one-shot sequence using (solid line) the stimulated antiecho and (dotted line) the stimulated echo. The diffusion delay Δ is the time between the

BPPSTE(stebpgp1s, ledbpgp2s, dstebpgp3s)

-> Required EXORCYCLE phase cycling (at least NS=8)

EXORCYCLE: Remove the effects of an imperfect refocusing pulse



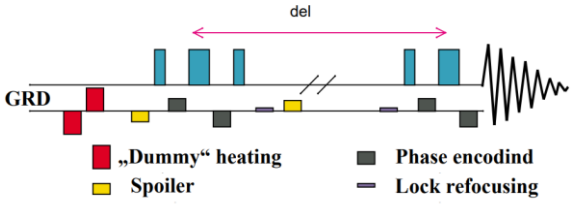


Figure 8. Oneshot DOSY Experiment

Remove the need for EXORCYCLE

-> Cyclops cycle

Retain the refocusing of chemical shifts and background field inhomogeneity

keep constant the **net energy** supplied to the gradient coil by the sequence for a **single transient (NS=1)**

Table 1. Phase cycling for the pulse sequences of Fig. 1(b)

ϕ_1	$0_4 1_4 + 02$
ϕ_2	$0_{128} 2_{128}$
ϕ_3	$0_{32} 2_{32}$
ϕ_4	$0_2 2_2 + 0_8 1_8 2_8 3_8$
ϕ_5	$0_{64} 1_{64} + 0_{16} 2_{16}$
ϕ_R	$\phi_1 - 2\phi_2 + \phi_3 - \phi_4 + 2\phi_5$ (solid line)
ϕ_R	$-\phi_1 + 2\phi_2 - \phi_3 - \phi_4 + 2\phi_5$ (dotted line)

Phases are notated as multiples of 90° (0 = 0°, 1 = 90°, 2 = 180°, 3 = 270°), with subscripts denoting repetition; thus the cycle $0_4 1_4 + 02$ corresponds to the sequence of phases 0°, 180°, 0°, 180°, 90°, 270°, 90°, 270° on successive transients.

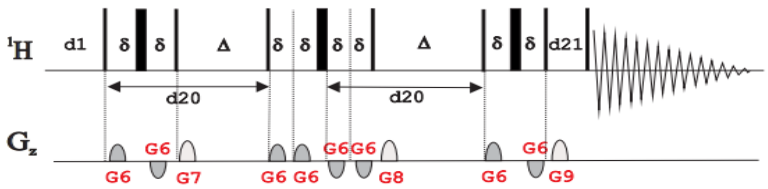
3. Standard Parameter Calibration

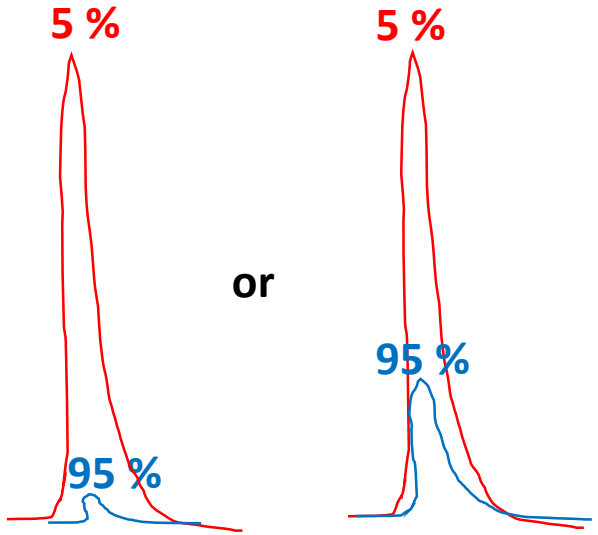
Parameters for Diffusion NMR

P1

Pulse width
Maximum Peak intensity
Phasing / Dephasing
DOSY sequence use many π/2 (90°), π (180°)

dstebpgp3s
dstebpgp3s1d





or

100 vs 5
Ideally

100 vs 20
for Low S/N

T1

AQ + D1 = T1 * 5
T1 > D20

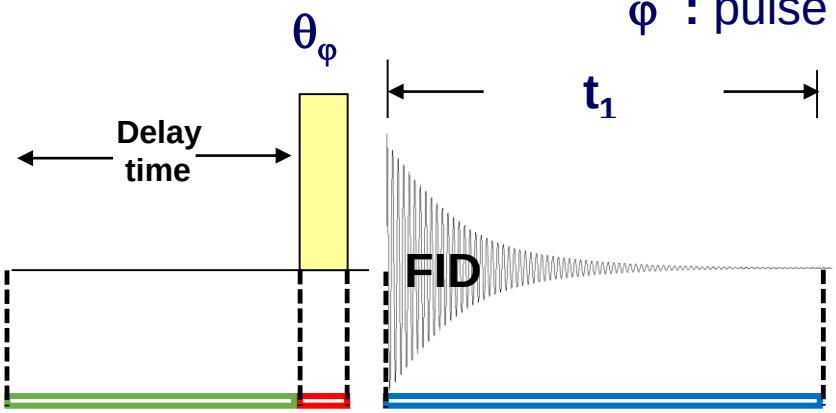
Big Delta, **D20**

Little Delta, **P30**

One pulse

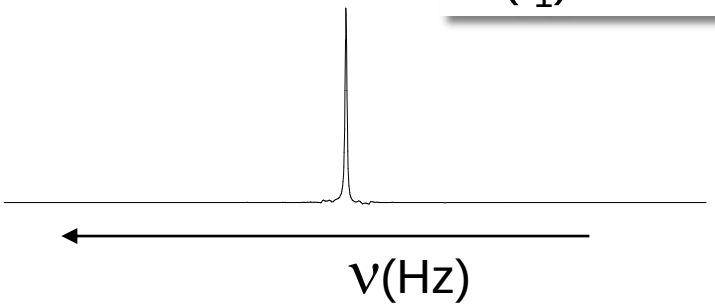
Basic 1D NMR

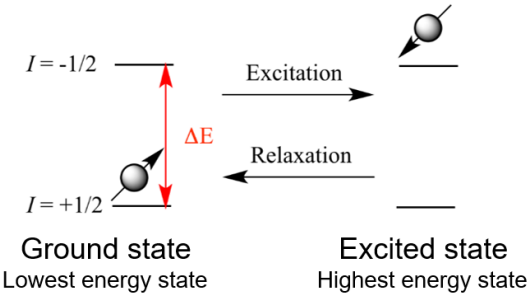
θ : pulse width(μs)
φ : pulse phase



Fourier Transformation

$$G(t_1) \xrightarrow{FT} g(f_1)$$





NMR

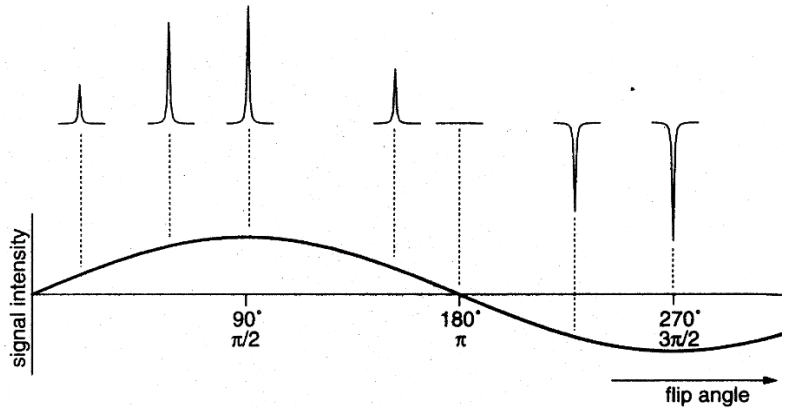
Parameter

- D1 (Relaxation delay time)
- P1 (Pulse width)
  PLW1 (Power level)
- AQ (Acquisition time)

Parameter calibration

1. Find P1

1) Type edc – create experiment room
2) Change PULPROG zg30 to **zg**
3) Set D1=10, P1=3, DS=0, NS=1
4) Type rga; zg
5) ProcPars -> Change pHmod no to pk
6) Type efp
7) Correct phase and save
8) Set P1=20 (About 180 °) or P1=40 (About 360 °)
9) Type efp -> Check peak phase (negative or positive)
10) Change P1 (negative -> decrease P1, positive -> increase P1)
    and find symmetry peak intensity (Exact 180 °)
11) Set P1/2 = 90 degree pulse (=Highest intensity)



1-1. Find P1 (with pulsecal)

1) Type edc – create experiment room
2) Change PULPROG zg30 to **zg**
3) Set D1=10, P1=3, DS=0, NS=1
4) Type ***pulsecal***

Parameter calibration

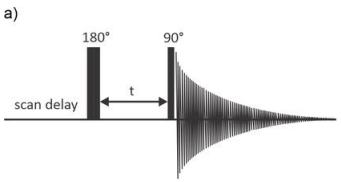
2. Find T1

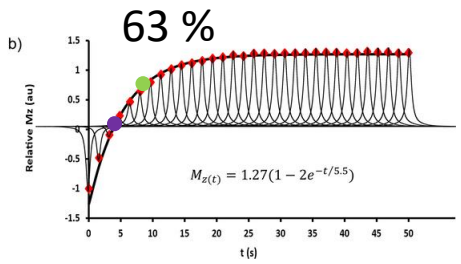
1) Type wrpa (ex. exp# 900)
2) Change PULPROG **t1ir**
3) Click AcquPars and change 1D to 2D
4) Set F1 domain TD=10 and set vdlist (ex, T1=20s)
5) Type ased
6) Set DS=0, NS= 1 or 2
7) Type rga; zg
8) Type xf2; abs2
9) Type rser 1 and correct phase and then **save 2d**
10) Type xf2; abs2
11) Click Analyse -> Dynamics -> T1/T2
12) Click Spectrum and put 1 at Slice number
13) Click Peak/Range and click manual integration
14) Export Regions o relaxation module and .ret
15) Click Relaxation and click fitting

2-1. Find D7null(T1)

1) Type wrpa (ex. Exp# 901)
2) Change PULPROG **t1ir1d**
3) Type ased
4) Set D7null=0.002(or 2m)
5) Type zg and efp
6) Check negative peak.
7) Find D7null value
   (zero intensity)

T1 * ln(2) = **D7null**
T1 = **D7null** * 1.443





4. DOSY Parameter Calibration

ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

DOSY parameters

D20	Diffusion delay	100 ms < T1 (shortest)
D21	Eddy-current delay	5 ms (typically)
P30	Gradient duration	500 – 3000 us (Usually 2500 us), P30/(D1+AQ) < 0.05 s
D16	Gradient recovery delay	200 – 1000 us (typically)
P19	Gradient length	600 us (0.6ms)
gpz6	Gradient ratio	5 – 95 %
gpz7	Spoil gradient	-17.13 %
GPNAM 6		SMSQ10.100 (smoothed rectangular shape)
GPNAM 7		SMSQ10.100 (smoothed rectangular shape)
NS	number of scans	8*n (Related Phase cycling for BP)
DS	dummy of scans	4*m
D1	Delay time	T1 * 3 – 5
TD1	Steps	16 (usually 16 ~ 32, Use ≥ 7)

P30 (Gradient duration)

P30 Gradient duration

Protect the probe -> Max gradient time is 10 ms

stegp1s

- **1 spoil gradient (0.6 ms)**
- **2 diffusion gradients (4.95 ms * 2)**
- GPZ6 : GPZ7(Spoil)

  100 : -17.13

  10 ms – 0.6 ms * 1 * 17.13 % = 9.90 ms

  9.9 ms / 2 = **4.95 ms**

ledbpgp2s

- **2 spoil gradients (0.6 ms * 2)**
- **4 diffusion gradients (2.41 ms * 4)**
- GPZ6 : GPZ7 (Spoil) : GPZ8 (Spoil)

  100 : -17.13 : -13.17

  10 ms – 0.6 ms * 2 * (17.13 % + 13.17%) = 9.64 ms

  9.64 ms / 4= **2.41 ms**

dstebpgp3s

- **3 spoil gradients (0.6 ms * 3)**
- **8 diffusion gradients (1.15 ms * 8)**
- GPZ6 : GPZ7 (Spoil) : GPZ8 (Spoil) : GPZ9 (Spoil)

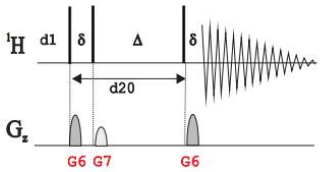
  100 : -13.17 : -17.13 : -15.37

  10 ms – 0.6 ms * 3 * (13.17 % + 17.13 % + 15.37 %) = 9.18 ms

  9.18 ms / 8 = **1.15 ms**

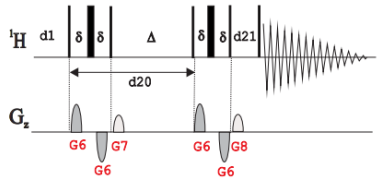
stegp1s

stegp1s1d



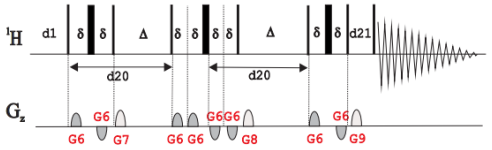
ledbpgp2s

ledbpgp2s1d



dstebpgp3s

dstebpgp3s1d



Diffusion Measurement

1. Find P1, AQ, D1(T1)
2. **Find D20 and P30 (Measure 1D DOSY)**
3. Measure 2D DOSY
4. Processing

1) Type ***wrpa*** exp # 10
2) Change pulprog to stepgp1s1d or dstepgp1s1d (1D DOSY)
3) Type ***gppp*** (automatically insert GPNAM6, GPANM7, etc..)
4) Set parameter D20, P30
5) Set parameter gpz6=95 (95%)
6) Type ***wrpa*** exp # 11
7) Set parameter gpz6=5 (5%)
8) Type ***re 10***; zg
9) Type ***re 11***; zg
10) Type ***ef*** or click processing spectrum – change ph mode to pk – type efp
11) Type ***re 10; efp; .md*** / Double click exp #11
12) Click right mouse button –> choice match intensities
    –> check intensity ratio 5% (0.05 or 20 times),
        Poor S/N ratio sample could 20% (0.2 or 5 times)
13) Change D20 or P30 until intensity ratio 5%

Diffusion Measurement

1. Find P1, AQ, D1(T1)
2. Find D20 and P30 (Measure 1D DOSY)
3. **Measure 2D DOSY**
4. Processing

1) Type ***wrpa exp*** # 100
2) Change pulprog to stepgp1s
3) Click AcquPars and change 1D to 2D
4) FnMODE = QF
5) Type ***gppp*** (Automatically write gradient parameters)
6) Set parameter D20, P30
7) Type ***xau dosy 5 95 16 l y y***

xau: macro
xau dosy: excute dosy macro
5: First gradient (gpz6)
95: Last gradient (gpz6)
16: TD (for F1), 16 steps
l: Linear lamp (Could choice q:square lamp, e: exponential lamp)
y: start acquisition
y: rga

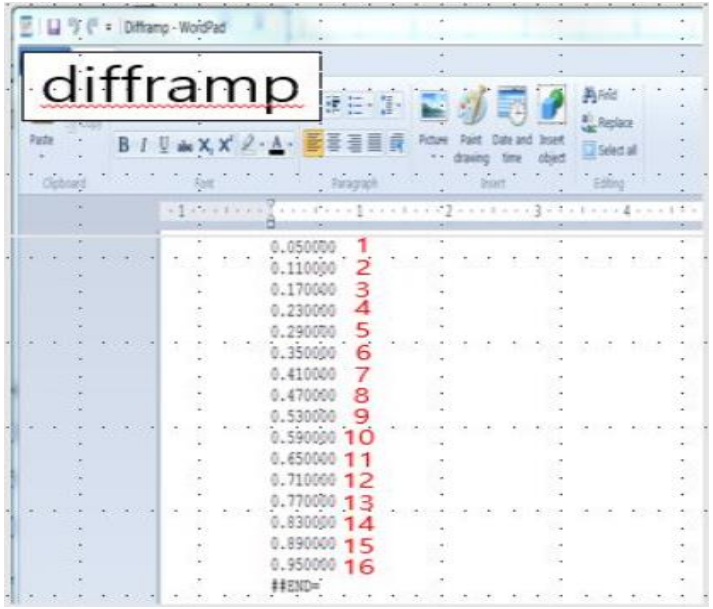
Class of gradient lamp

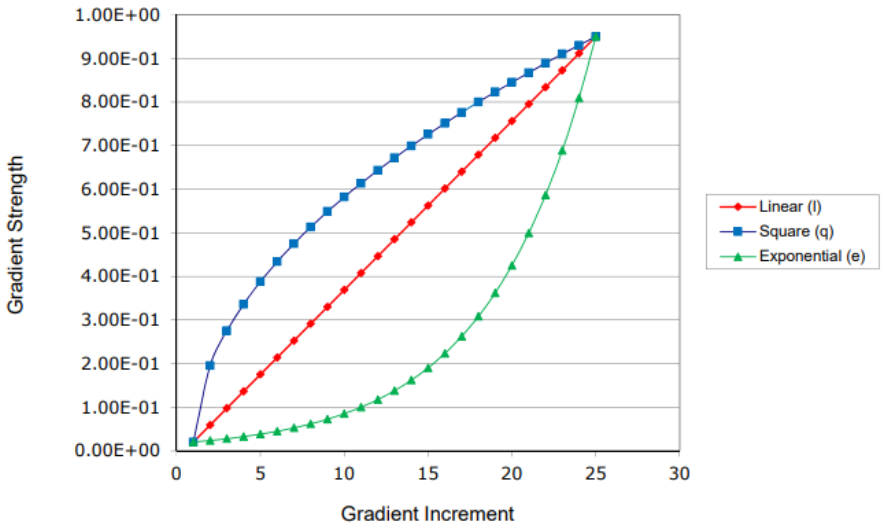
Class of gradient lamp

- l: Linear lamp
- q: Square lamp
- e: Exponential lamp

- Difframp -> Normal gradient
- DifframpR -> Reverse gradient

(C/bruker/topspin/exp/stan/nmr/list/gp/user)





Special technique

Special technique

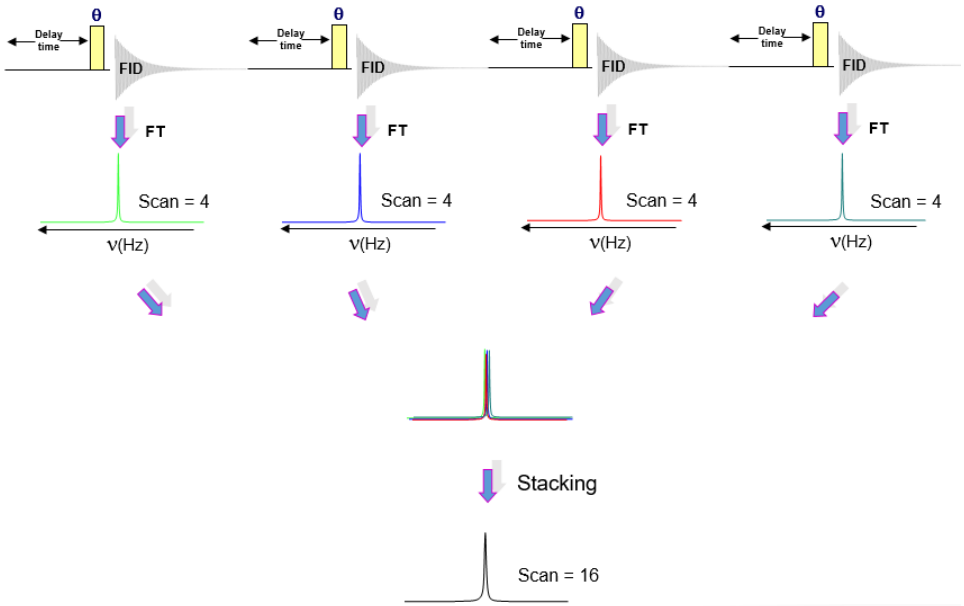
1. Random diffusion (Use NUS)

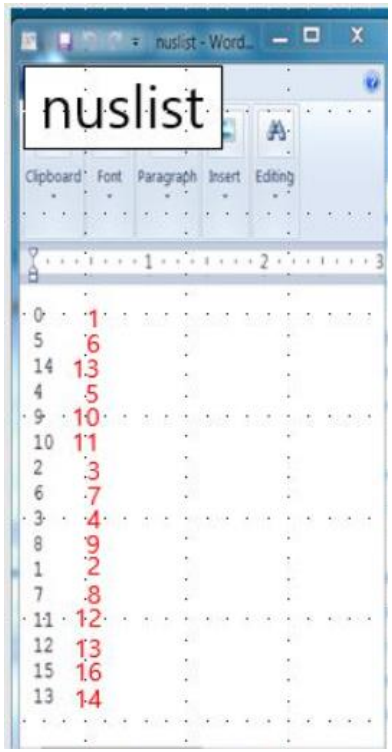
- Set FnType to “Non-uniform sampling”
- Set NUSamount to 100%
- Set NusSPTYPE to 3

2. Tdav (= interleaved in Varian)

If we set Tdav = 4, NS=16, it works like

-> Improve diffusion data accuracy





Processing

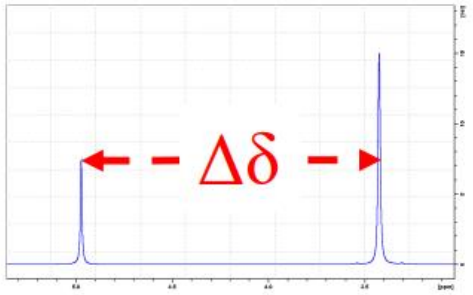
1. Find P1, AQ, D1(T1)
2. Find D20 and P30 (Measure 1D DOSY)
3. Measure 2D DOSY
4. **Processing**

1) Type ***xf2; abs2; setdiffparm***
2) Analyse -> T1/T2 -> FID -> Spectrum -> 1
3) T1/T2/ -> Peaks/FID -> Integration -> Save to relaxation module
4) Relaxation -> **>>**

5. Temperature Calibration

Temperature Calibration

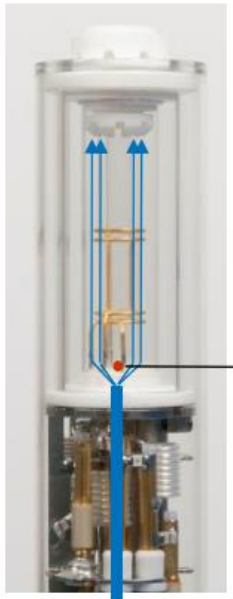
- The VT Sensor can be calibrated for accurate sample temperature values
- The –OH of MeOH is temperature sensitive



Neat Methanol

$T\,[K] = 409.0 - 36.54\,\Delta\delta - 21.85\,(\Delta\delta)2$

- The AU program **calctemp** measures the splitting and determines actual sample temp



Sensor
Thermocouple
Pt-100

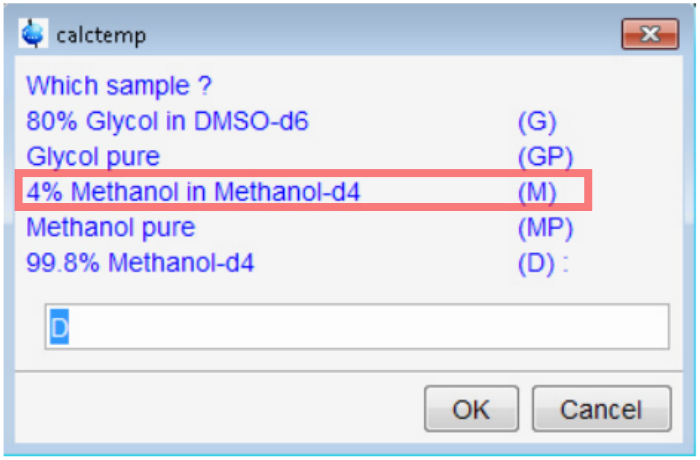
Heater

VT Unit

J. Magn. Reson. **1982**, *46*, 319-321

Temperature Calibration

Temperature Calibration - calctemp



- High Temp = Ethylene Glycol
  - ✓ 300-380 K
- Room/Low Temp = Methanol
  - ✓ 180 – 330K

➢ Cryoprobes especially 99.8% Methanol-d4

Temperature Calibration

Ethylene Glycol is useful for temperatures from ~300K to 380K

Source: Bruker Instruments, Inc. VT-Calibration Manual

80% Ethylene Glycol (DMSO-d6): $T = (4.218-\Delta)/0.009132$
100% Ethylene Glycol: $T = (4.637-\Delta)/0.009967$

(Δ is the shift difference (ppm) between CH_2 & OH peaks)

Methanol is useful for temperatures from ~180K to 300K

Source: Bruker Instruments, Inc. VT-Calibration Manual

100% Methanol: $T = -23.832\Delta^2 - 29.46\Delta + 403.0$

(Δ is the shift difference (ppm) between CH_3 & OH peaks)

100% d4-Methanol, Deuterium Observe
(Source: Experimental Data: Univ. Nebraska, 2001)

$$T = -23.1902\Delta^2 - 31.1062\Delta + 399.081$$
where Δ = ppm(OD) vs. ppm (CD_3)

Source: Bruker Instruments, Inc. VT-Calibration Manual
4% Methanol in Methanol-d4:
180-300K, $T = (3.86 - \Delta)/0.00782$ (approximate)

for more accurate values, use the following, depending on T:
180-230K, $T = (3.72 - \Delta)/0.007143$
230-270K, $T = (3.92 - \Delta)/0.008$
270-300K, $T = (4.109 - \Delta)/0.008708$

(Δ is the shift difference (ppm) between the CH_3 and OH peaks)

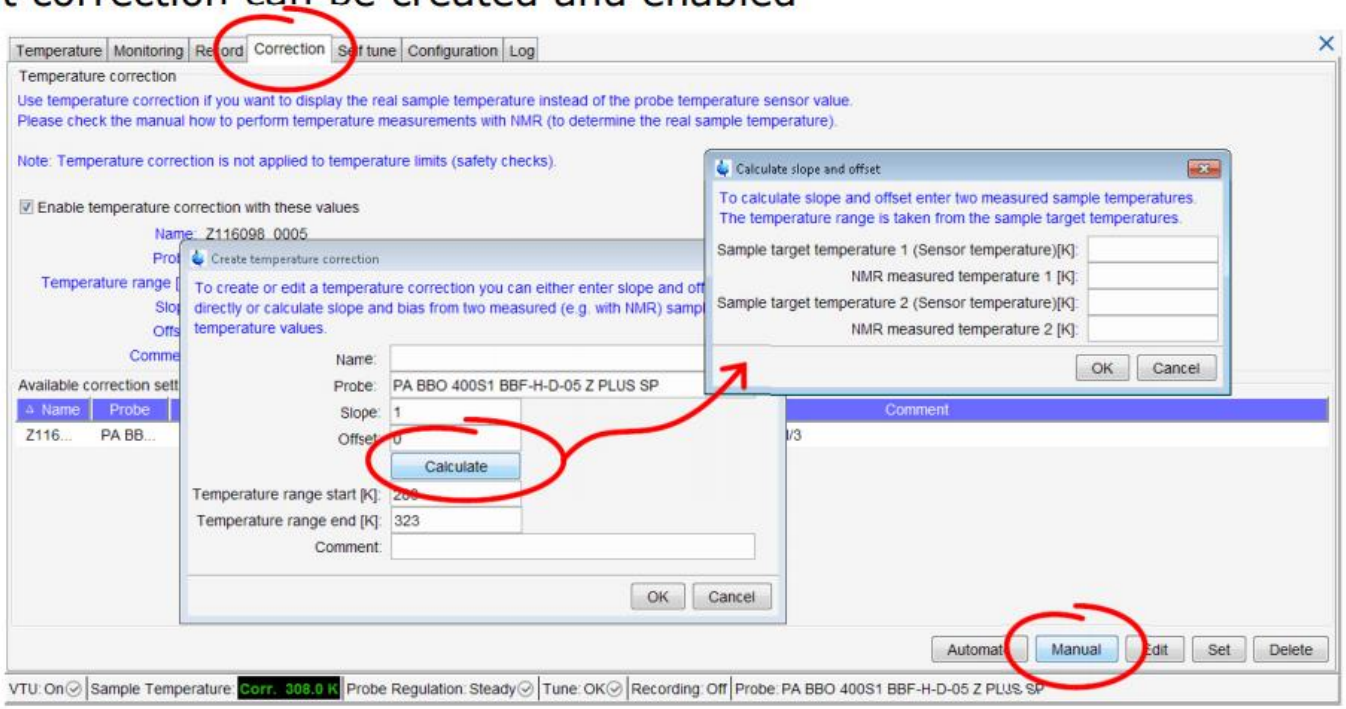
http://staff.ustc.edu.cn/~liuyz/methods/NMR_VT_calibration.htm

Temperature Calibration

Temperature Calibration / Correction

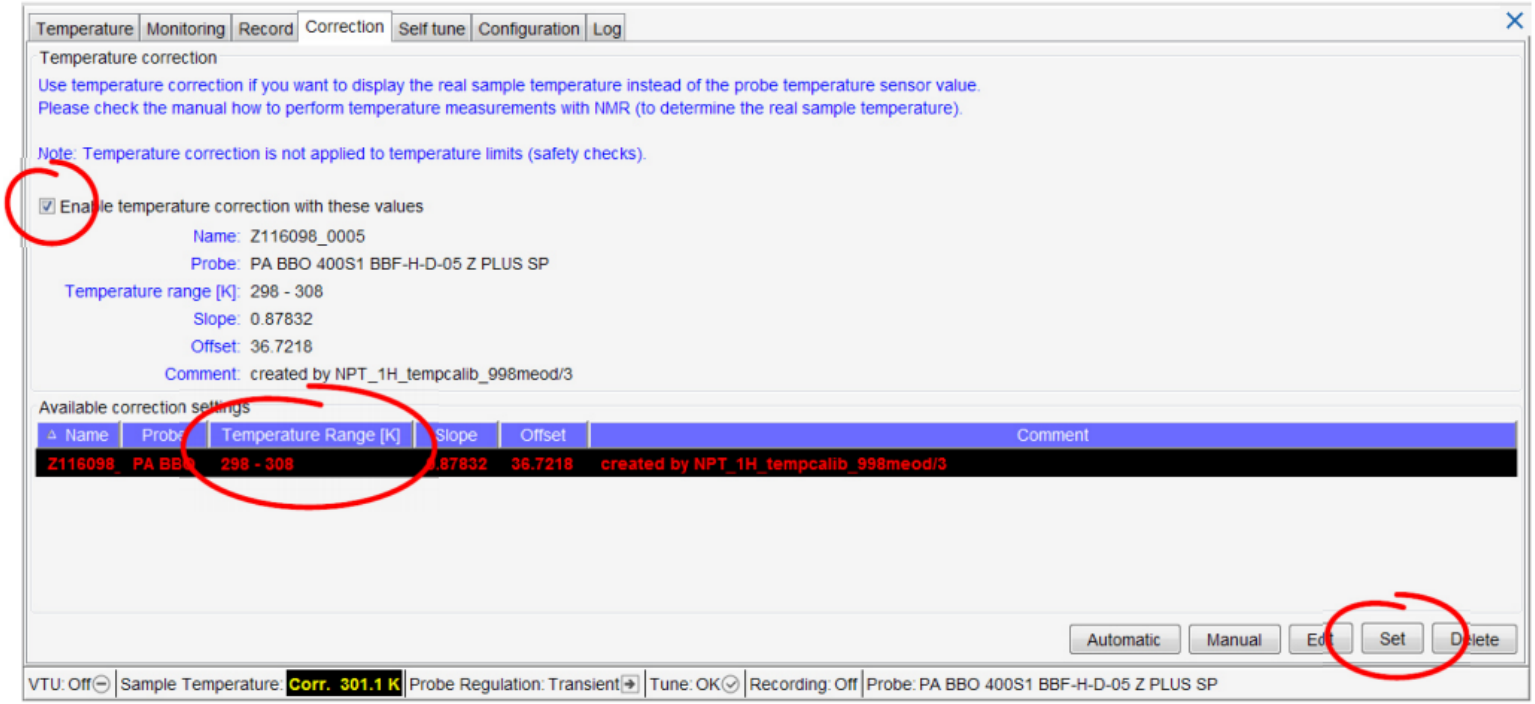
A simple 2 point correction can be created and enabled

1. Set and measure the temperature at 2 targets
2. Suggest 30 – 40 degrees apart.
3. This is the correction for this range
4. Add another correction for other ranges



Temperature Calibration / Correction

Enable the correction appropriate for your temperature range



6. Gradient Calibration

Gradient Calibration

Calibration Procedure for a Single Axis Gradient System

$$GCC_{new} = GCC_{old}\sqrt{\frac{D}{D_{Literature}}}$$

Type gradpar
Initial value = 5.35 G/cm
Find proper gradpar value
(Doped water = 1.913 on RT)

2.4.6 Preparation for NMR Adjustments

It is highly recommended to use the doped water sample (Z10906) for all setup experiments. If this sample is not available, a similar sample consisting of 1% H_2O in D_2O, plus 0.1% $CuSO_4$ should be prepared. The exact concentration is not important for the pre-emphasis adjustment, but it is useful for the later gradient calibration. Low concentrations of H_2O are important in preventing radiation damping. The $CuSO_4$ is mainly used to save time, but it also helps prevent radiation damping. The sample filling height should be about 40 mm.

1.1. Product identifier

NMR-SAMPLE 0,1 mg GdCl3/ml D2O + 1% H2O +0,1% CH3OH 13C (DOPED WATER)

Further trade names

NMR-SAMPLE 0,1 mg GdCl3/ml D2O + 1% H2O +0,1% CH3OH 13C (DOPED WATER):
Z100933, Z10727, Z10046, Z10083, Z10906, Z10085
Z10082, Z10084, Z10916
NMR-SAMPLE 0,1 mg GdCl3/ml D2O + 1% H2O (DOPED WATER):
Z10047, Z10088, Z10090
Z10087, Z10089

Gradient Calibration

Nucleus	Sample	Temperature [C]	D [$10^{-9}m^2/s$]
^1H	H_2O	20	2.031
^1H	H_2O	25	2.299
^1H	D_2O	25	1.872
^1H	"Doped Water"	25	1.91
^1H	DMSO	25	0.730
^7Li	0.25 m LiCl in H_2O (ca. 10 g LiCl /l H_2O)	25	0.960
^{23}Na	2 m NaCl in H_2O (ca. 117 g NaCl / l H_2O)	25	1.135

Table 2.3: **Some useful diffusion coefficients**

$$D(x_D) = (2.3 - 0.4652 \cdot x_D + 0.0672 \cdot x_D^2) \cdot 10^{-9} \frac{m^2}{s}$$

$$x_D = mole\ fraction\ of\ deuterons$$

Figure 2.25: Equation 1

[* Calibration in Accurate Spin-Echo Self-Diffusion Measurements Using 1H and Less-Common Nuclei, Holz et al., *JMR 92*, 115-125 (1991)].

Non-linearity of the gradient

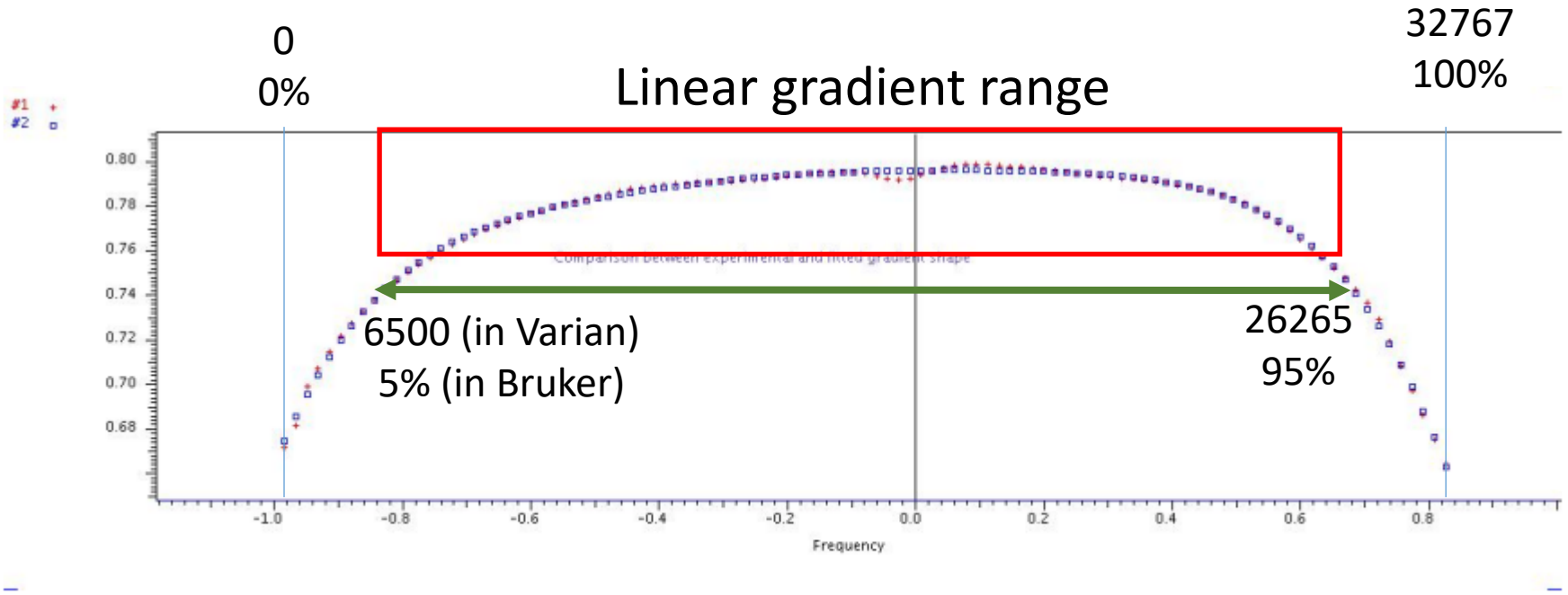


Figure 7 Typical comparison between the experimental and fitted gradient shape produced by the probe.

Limitation of measurement

Probe		Gradient	T1, T2 limit	Estimation limit
BBO	Bruker	0.05 T/m		$< 3 \times 10^{-11}$ m²/s
AutoX-DB	Varian	0.06 T/m		$< 2.8 \times 10^{-11}$ m²/s
DiffBB	Bruker	17 T/m		$< 1 \times 10^{-14}$ m²/s
Diff30	Bruker	18 T/m	T1 > 1 s, T2 > 100 ms	$< 9.4 \times 10^{-15}$ m²/s
Diff50	Bruker	30 T/m	T1 > 0.56 s, T2 > 56 ms	$< 5 \times 10^{-15}$ m²/s
DOTY Diff	DOTY	33 T/m	T1 > 0.504 s, T2 > 50.4 ms	$< 4.5 \times 10^{-15}$ m²/s

PROBES

DiffBB

The DiffBB is a broadband gradient probe with the Automatic Tuning Module (ATM) for NMR diffusion investigations of a wide range of diffusivities. 10-8 to 10-13 m2/s (10-15 m2/s under favorable sample conditions).

PFG/Diffusion Liquids Z Gradient Probes-Pulsed Field Gradient Coils 0ver 3,300 G/cm (33 T/m)

We have a new version of our PFG probe that can extend sample **temperatures up to +300C.** For recent experimental results: *"Temperature Dependence of the 13C NMR of Nylon 6,6 —Liquids- Z Gradient Probe up to 300°C"*

For Information on Diffusion Techniques: *"A Practical Guide to Setting Up Diffusion Measurements Utilizing Pulsed Field Gradients"*

Introduction | Specifications | Oscillating Gradient Spin Echo (OGSE)

Highest Efficiency, Ultra-Shielded, Fastest Switching

- Measure the lowest diffusion coefficients — to 10^{-15} m²/s

Check list

Before Your DOSY,

1. Check Temperature Calibration !!

<DOSY Standard sample>

- Doped (0.1mg/ml GdCl3) 1% H2O in D2O sample

- **Diffusion coefficient (different temp.)**
  25.0 °C = 1.913 * 10^-9 m²/s
  25.1 °C = 1.918 * 10^-9 m²/s
  25.2 °C = 1.923 * 10^-9 m²/s

2. Check Gradient Calibration

3. Check Solvent

- CDCl3 = Low viscosity = Strong Convection