NMR magnetometry with single-chip RF transceivers

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Magnetic Resonance Domain

NMR

Nuclear Magnetic Resonance

→ **Weakly coupled nuclear spins**

ESR

Electron Spin Resonance

→ **Weakly coupled electron spins**

FMR

Ferromagnetic Resonance

→ **Strongly coupled electron spins**

NMR: Resonance frequency

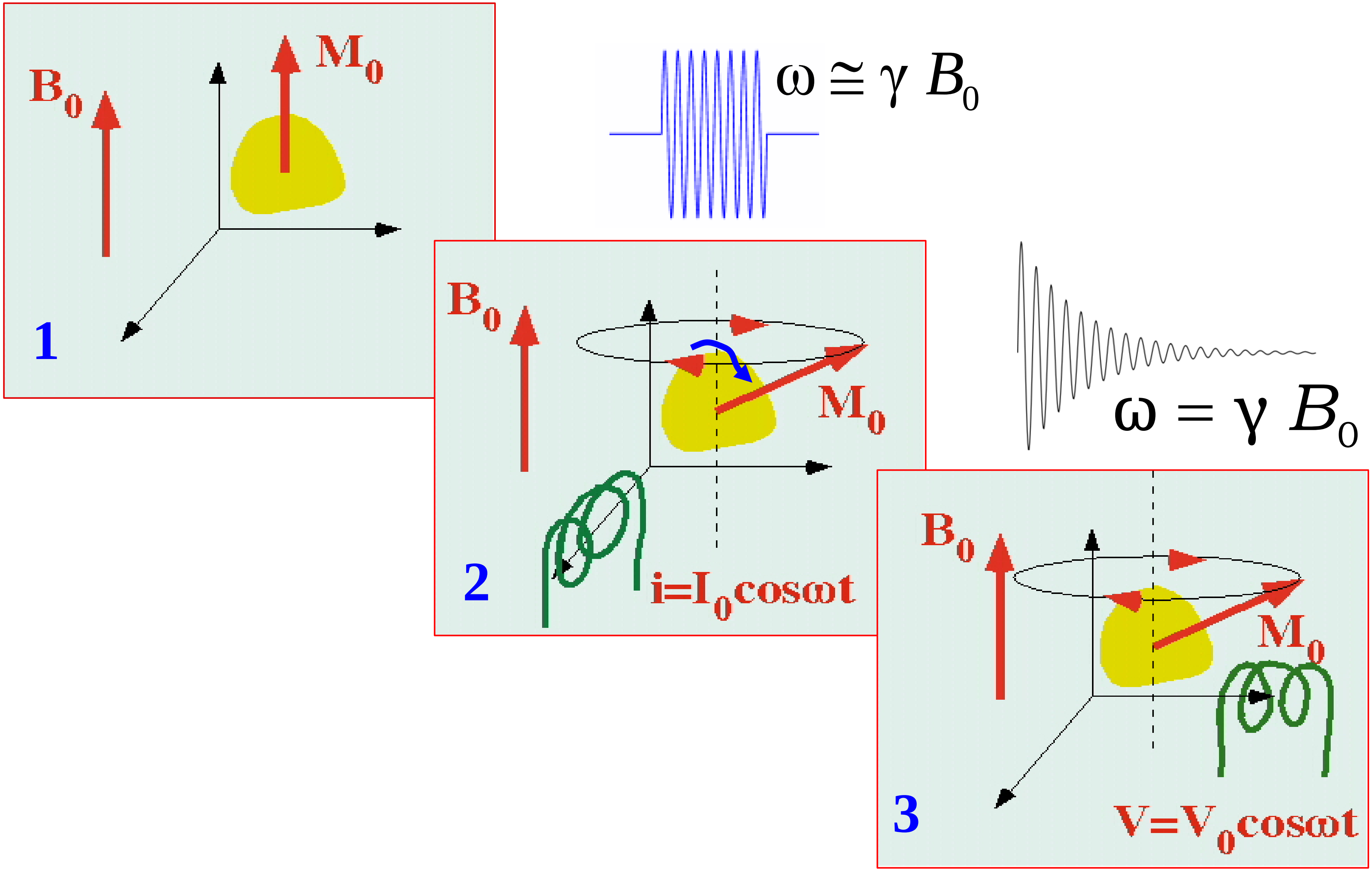
Many **nuclei** have a non-zero **magnetic moment**.

Nucleus	Spin I	Natural Abundance	Magnetic Moment (μ/μ_N)	Gyromagnetic Ratio γ (10^7 rad/s T)	Resonance Frequency (MHz/T)
^{1}H	1/2	99.9885	4.84	26.75	42.576
^{2}H	1	0.0115	1.21	4.11	6.536
^{13}C	1/2	1.07	1.22	6.73	10.705
^{17}O	5/2	0.038	2.24	3.63	5.772
^{19}F	1/2	100	4.55	25.2	40.052
^{31}P	1/2	100	1.96	10.8	17.235
……	…….	……	……	…….	……

$$\text{Nuclear Magneton } \mu_N = \frac{e\hbar}{2m_p} \cong 5 \times 10^{-27} \text{ J/T}$$

$$\text{Electron Magneton } \mu_B = \frac{e\hbar}{2m_e} \cong 9 \times 10^{-24} \text{ J/T}$$

NMR: simple experiment



NMR: signal and noise (inductive detection)

Signal (t=0):

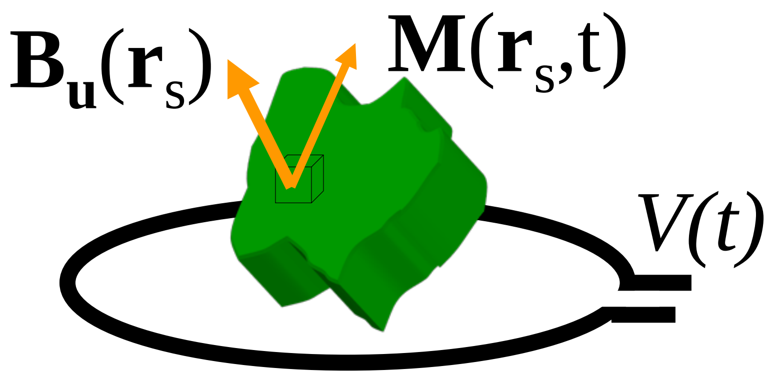
$$V_0 = M_0 V_S B_u \omega_0$$

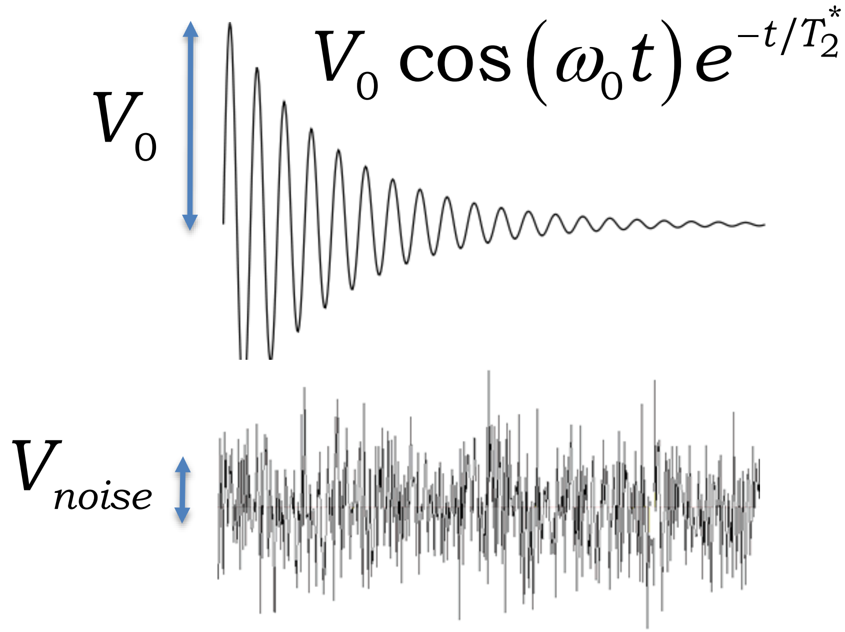
Noise:

$$V_{noise,rms} = \sqrt{4kTR\Delta f}$$

Signal-to-noise ratio:

$$SNR = \frac{M_0 V_S B_u \omega_0}{\sqrt{4kTR\Delta f}}$$





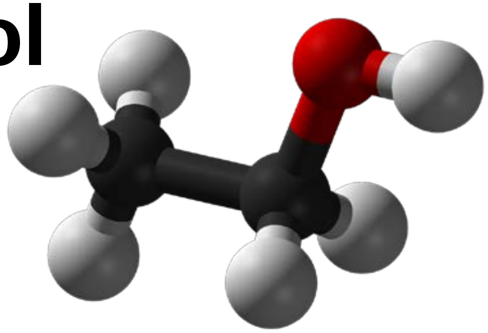
NMR: main applications

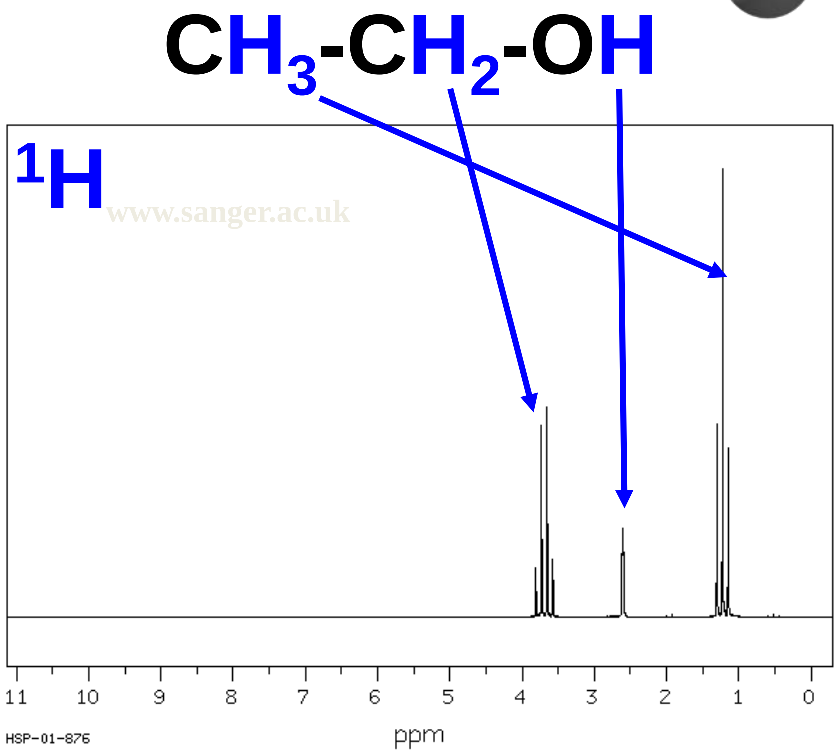
Molecular Structure Determination

3D Imaging

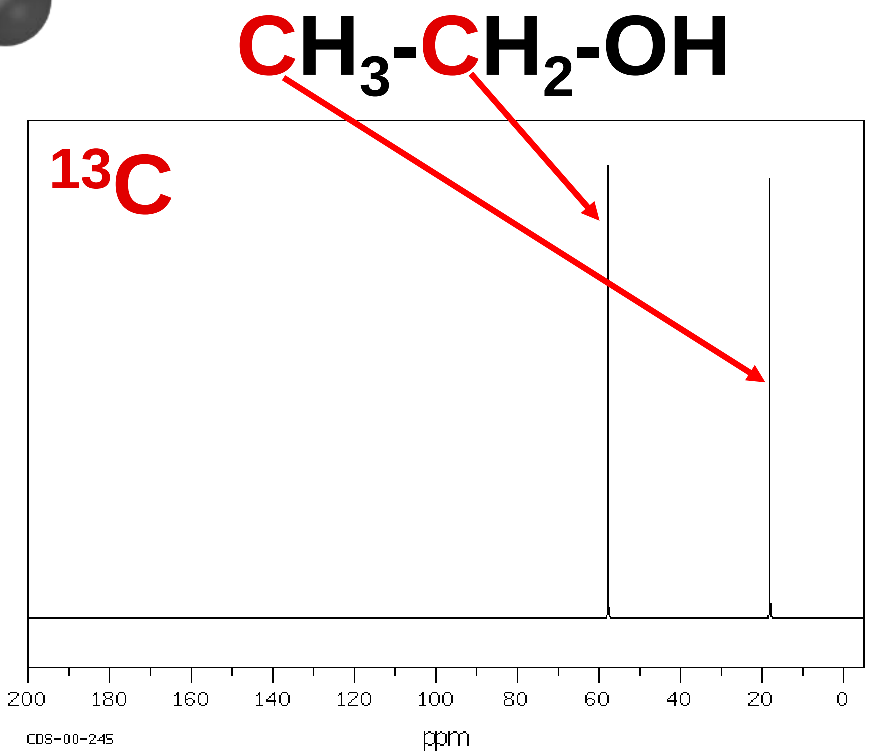
NMR of SMALL molecules

Ethanol



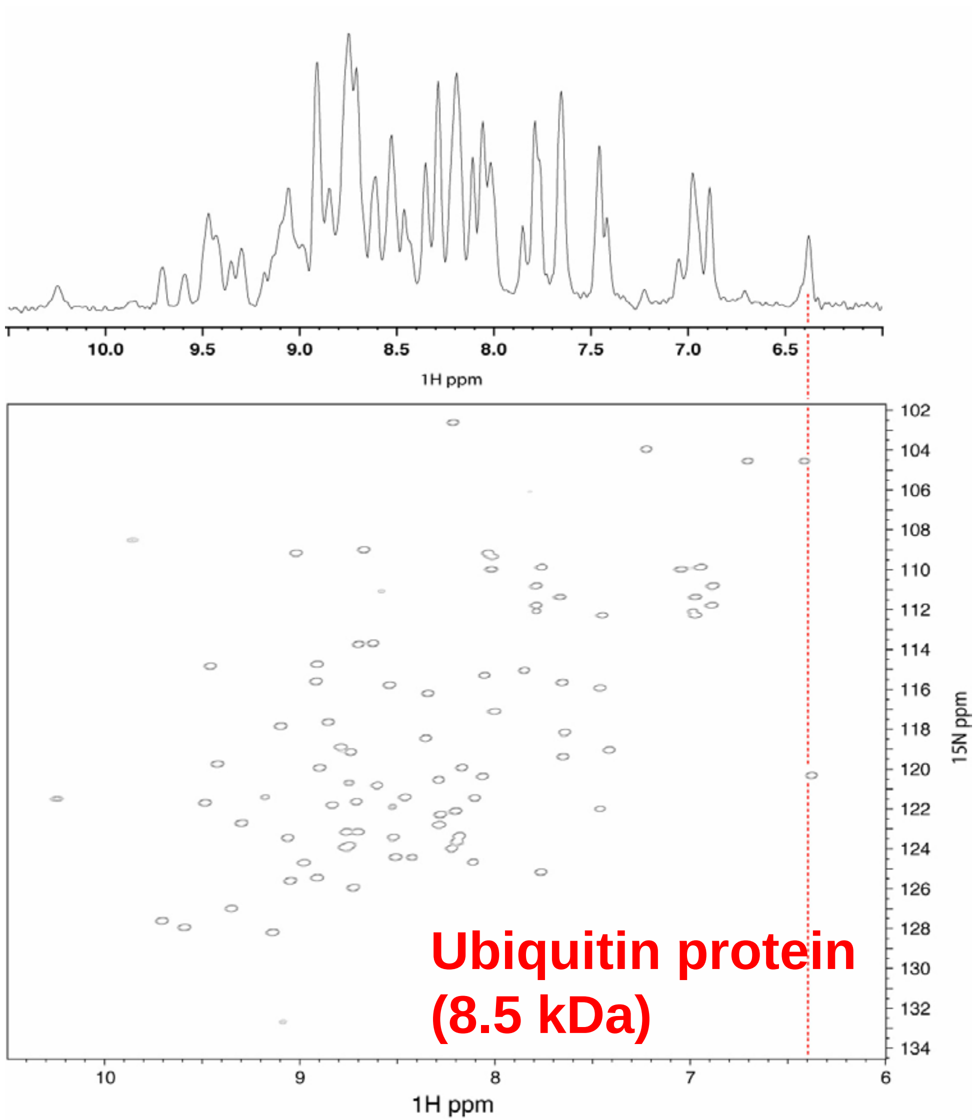


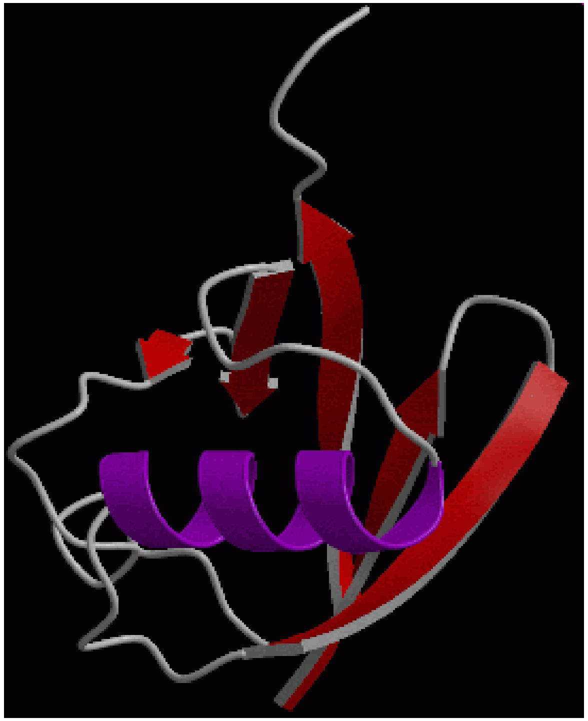
^{1}H: 43 MHz/T



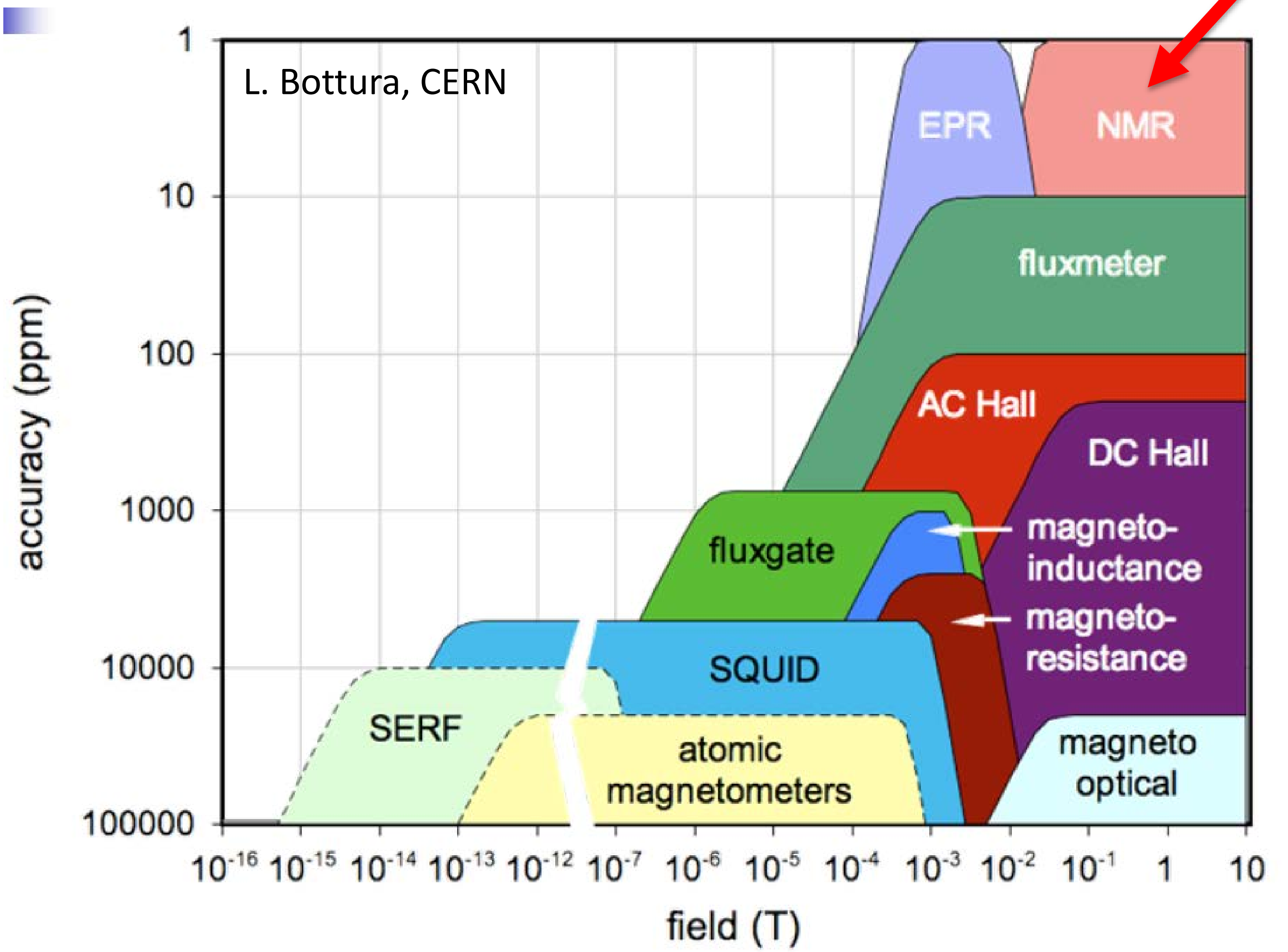
^{13}C: 11 MHz/T

NMR of LARGE molecules (up to 500 kDa)





NMR magnetometry



NMR magnetometry key-features

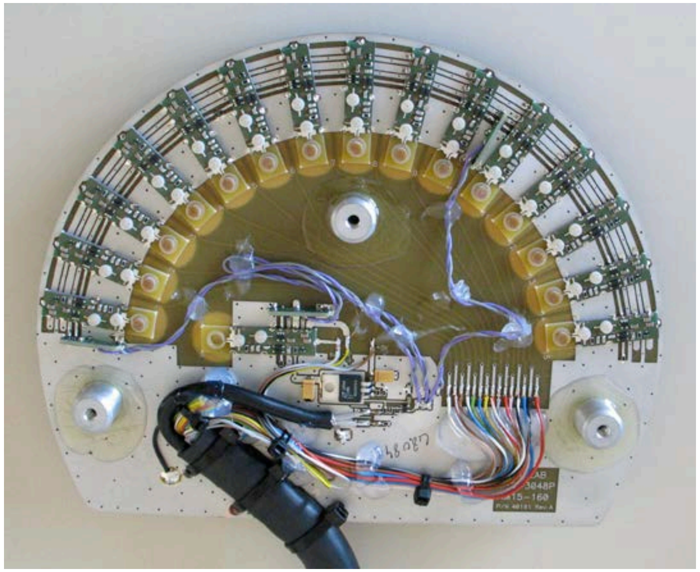
	Typical...	Best....
Field range	10 mT to 30 T	1 μT to 100 T
Accuracy	10 ppm	10 ppb
Resolution	100 ppb/$Hz^{1/2}$	0.001 ppb/$Hz^{1/2}$
Temperature range	280 K to 310 K	sub-K to 1000 K

NMR magnetometry: Applications

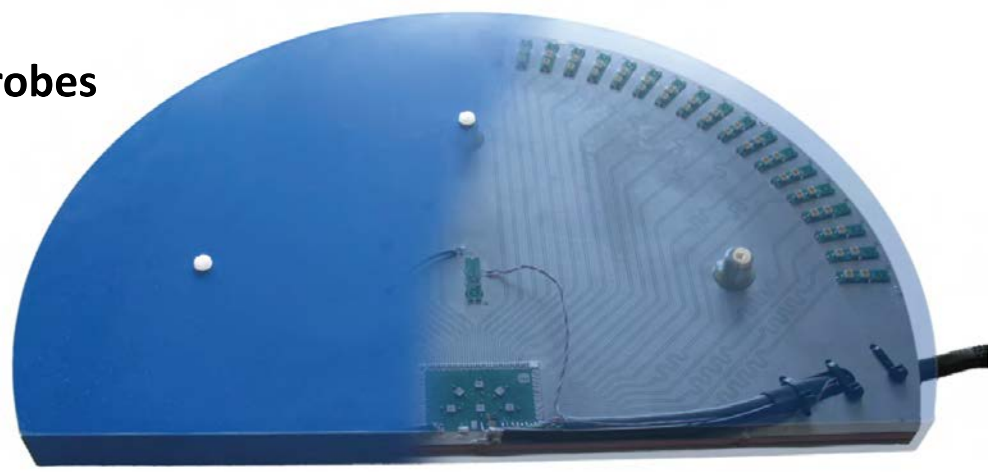
Application	When	By whom
Magnetic resonance imaging (MRI) magnets	During **fabrication** During **installation** in hospitals After **quenching** in hospitals After **room changes** in hospitals	General Electrics Philips Toshiba …….
Particles accelerator magnets	During **fabrication** During **operation**	CERN Fermilab DESY KEK Argonne PSI/SLS ….
Ordinary electromagnets and permanent magnets	**Calibration** Hall sensors Physics **experiments** …….	Hall sensors companies University labs ….

Metrolab NMR magnetometer (Array)

16 probes



40 probes



Metrolab

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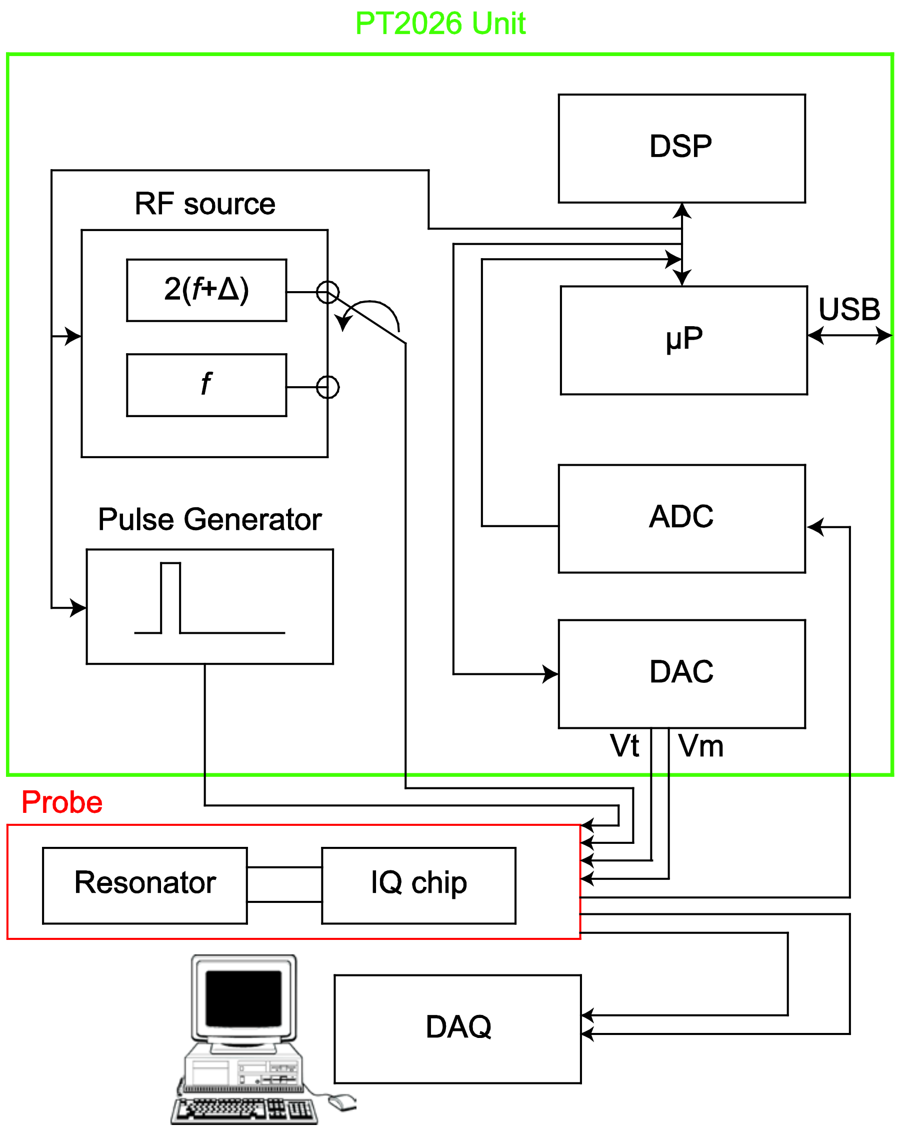
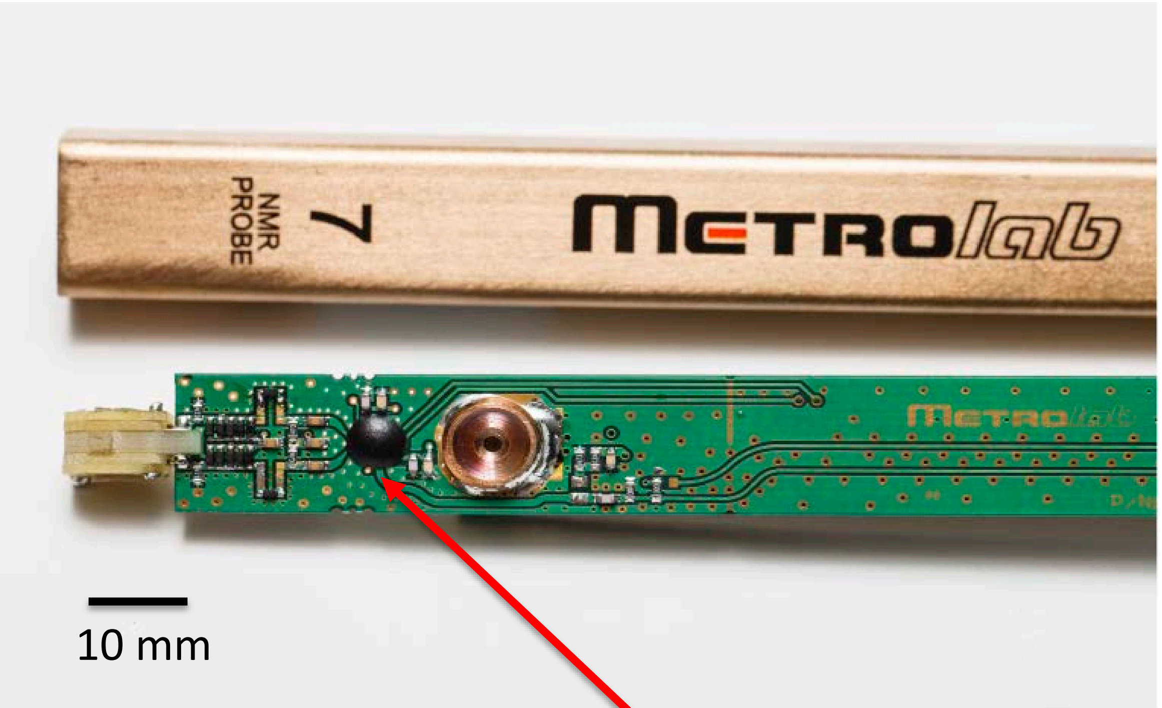
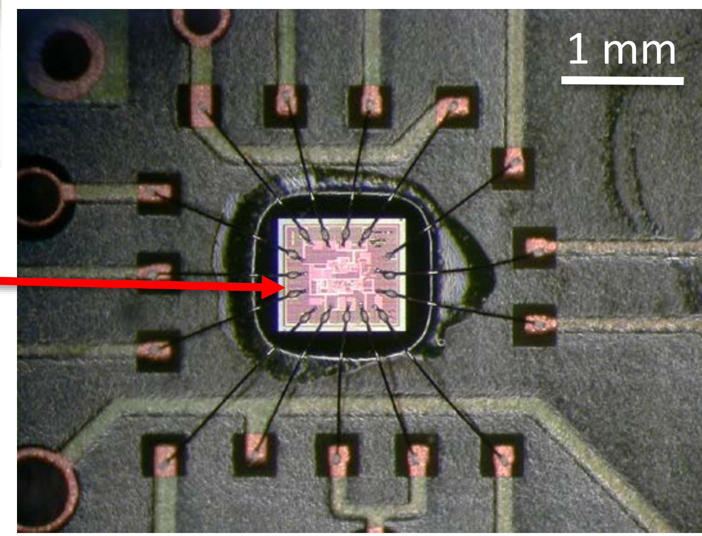
Metrolab NMR magnetometer (modified)



Metrolab probes with single-chip transceiver





Single chip CMOS transceiver

Why a single chip integrated transceiver ?

Single-chip Integrated Transceiver VS Discrete Components Transceiver
(for NMR magnetometry)

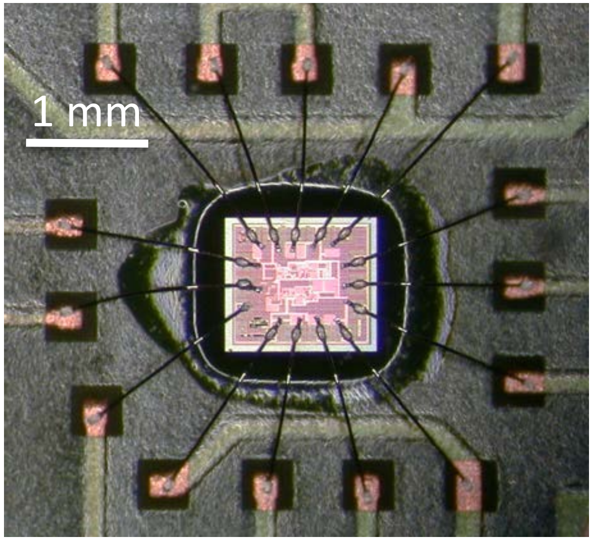
No search of many **non-magnetic components**.

Broadband operation with marginal compromise in noise figure.

Much smaller **size**.

Better or equal **SNR** and **magnetic field resolution**.

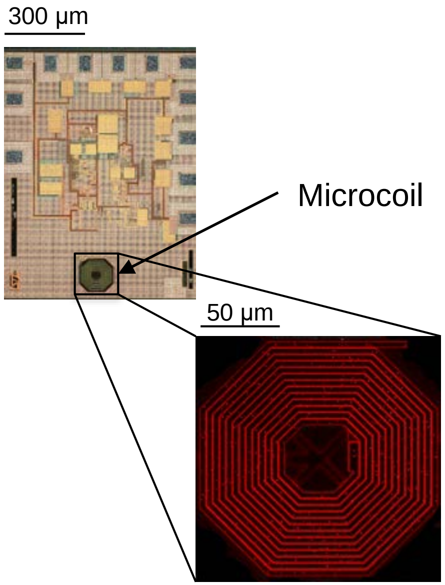
Single-chip transceivers

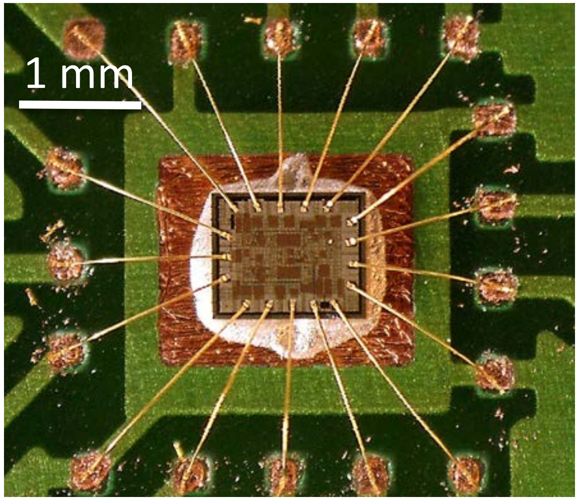


Chips area: about 1 mm^2

Single chip
I-only transceiver

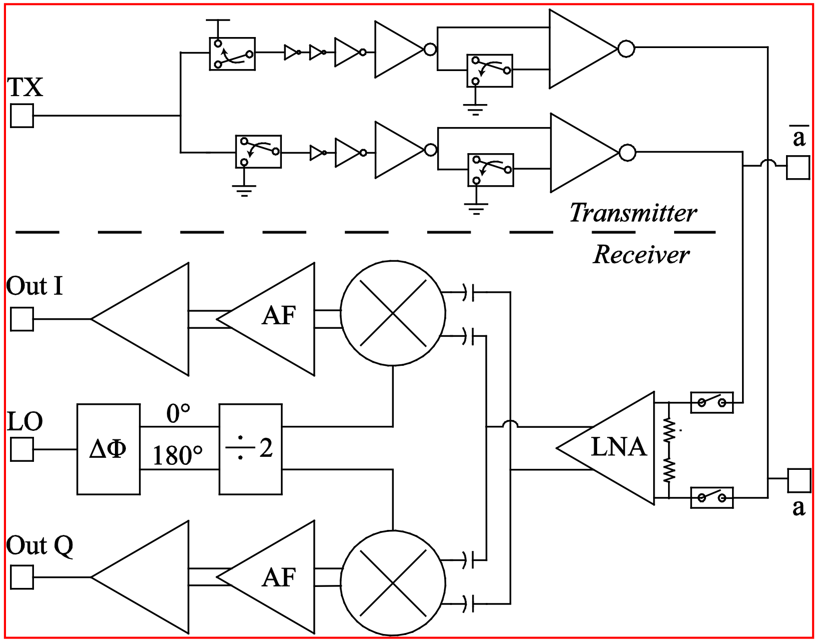
Single chip
I-only transceiver
(with integrated coil)



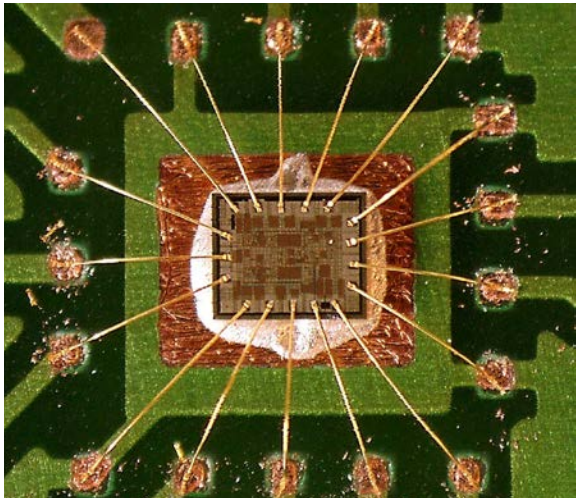


Single chip
IQ transceiver

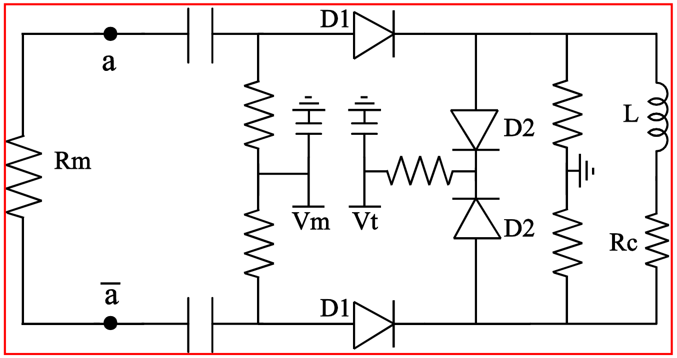
Single-chip IQ transceiver (with external resonator)



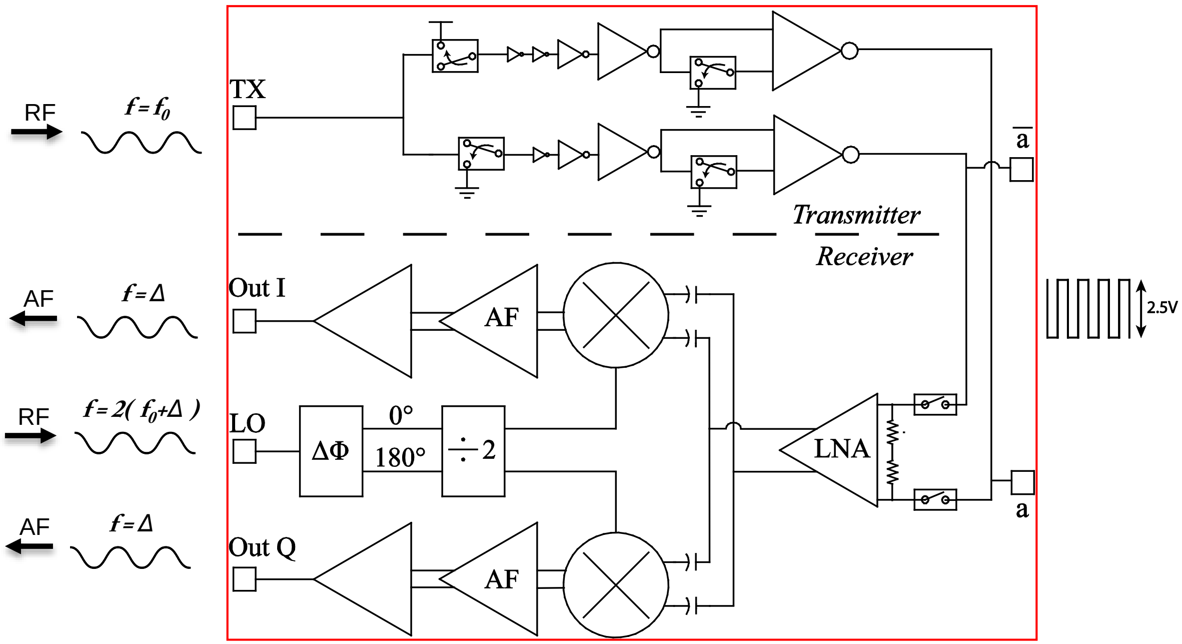
Single-chip IQ transceiver



External resonator



Single-chip IQ transceiver: details



- TX RF Input: -3 dbm
- TX RF Output: ~10 mW
- TX Bandwidth: 3-1200 MHz

- TX/RX recovery time: ~ 1 µs

- RX Bandwidth: 3-300 MHz
- RX Input noise: 1.1 $nV/Hz^{1/2}$
- RX Gain: 54 dB

- IQ error: 3° at 3 MHz
  0.1° at 1 GHz

- Power cons. ~20 mW

Field range

$$SNR = \frac{M_0 V_S B_u \omega_0}{\sqrt{4kTR\Delta f}}$$

To measure a **small B_0:**

- Large sample volume
- Dynamic nuclear polarization
- Polarization at an higher field (flowing sample)
- Non-inductive detection methods

Accuracy: accurate «calibrations»

Free proton :

$$f_0 = \frac{\gamma}{2\pi} B_0$$

$$\frac{\gamma}{2\pi} = (42.577\ 478\ 92 \pm 0.000\ 000\ 29)\,\mathrm{MHz/T}$$

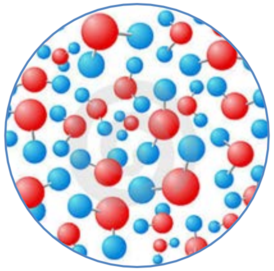
$$\pm\ 7\ \mathrm{ppb}$$

Proton in a spherical sample of pure water at 25 °C :

$$f_0 = \frac{\gamma}{2\pi}(1-\sigma)B_0 = \frac{\gamma'}{2\pi} B_0 \qquad \sigma = (25.691 \pm 0.011) \times 10^{-6}$$

$$\frac{\gamma'}{2\pi} = (42.576\ 385\ 07 \pm 0.000\ 000\ 53)\ \mathrm{MHz/T}$$

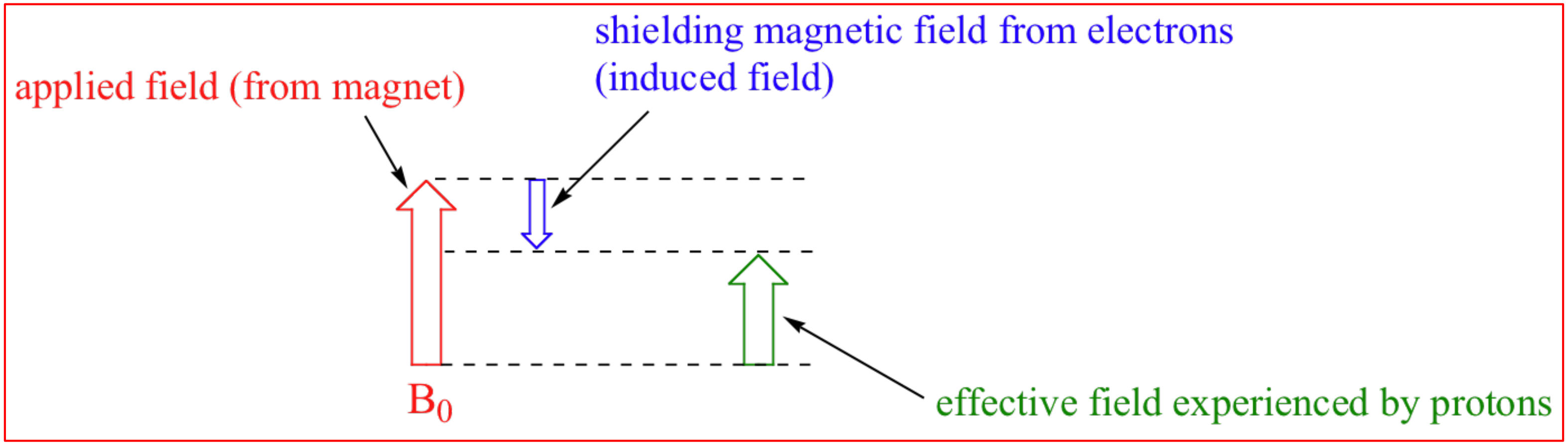
$$\pm 13\ \mathrm{ppb}$$

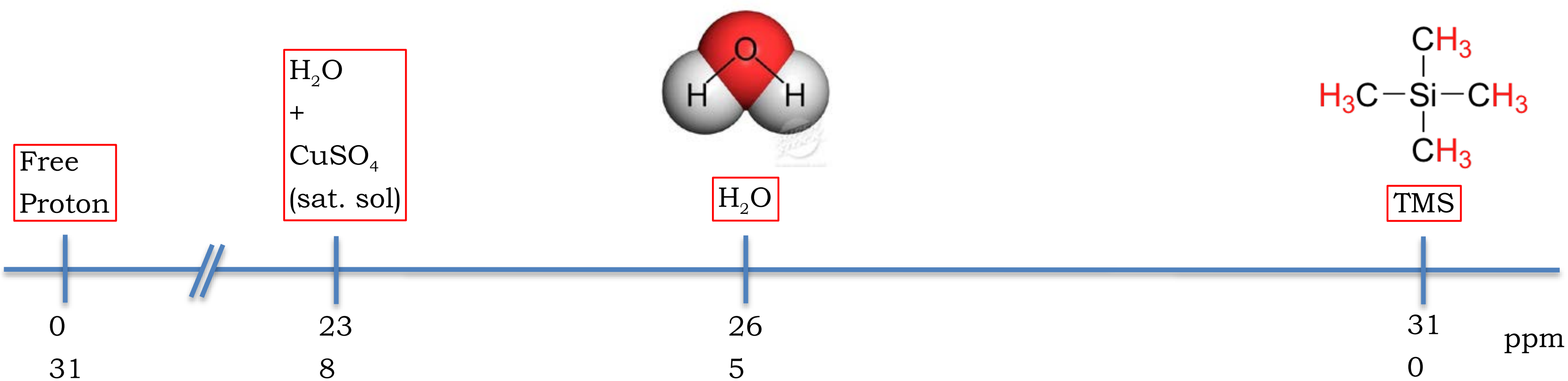


Accurate "calibrations"
0.01 ppm

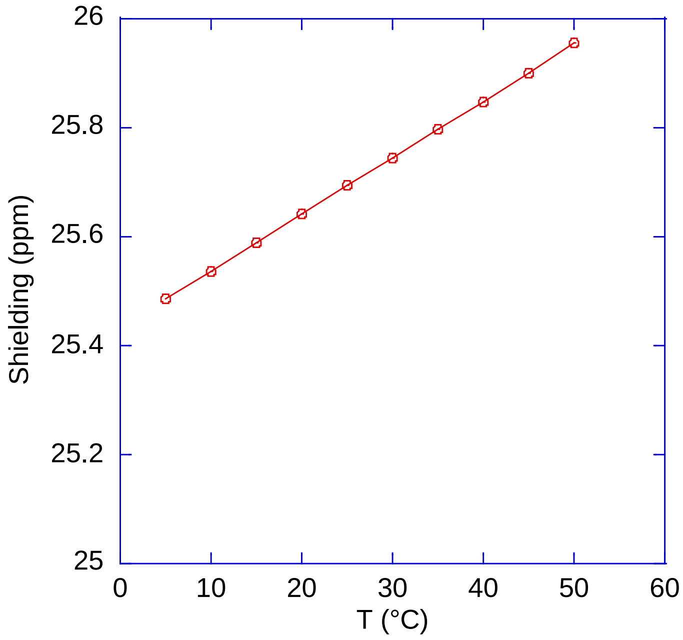
CODATA 2014

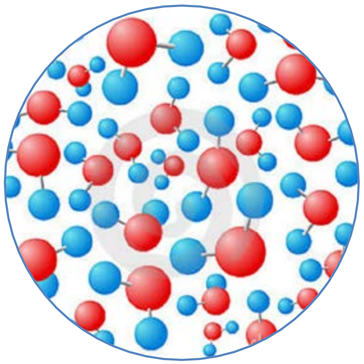
Accuracy: chemical shift





Accuracy: Temperature dependence



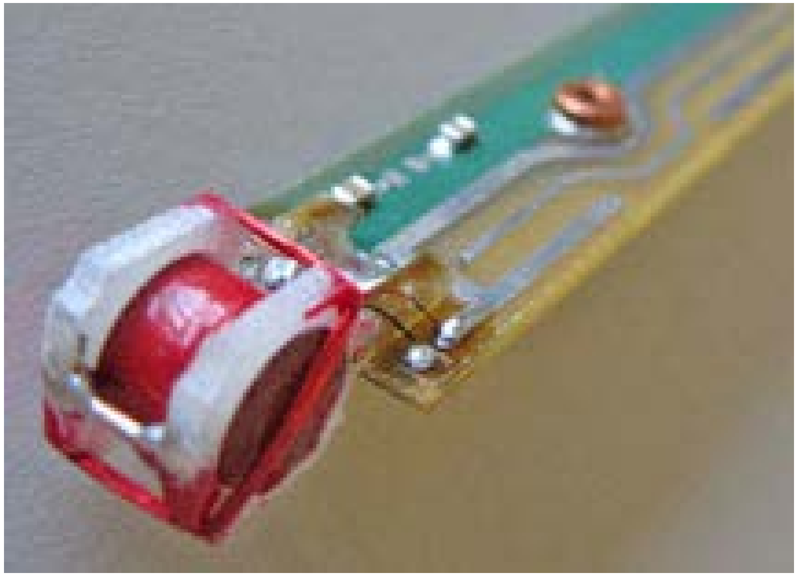


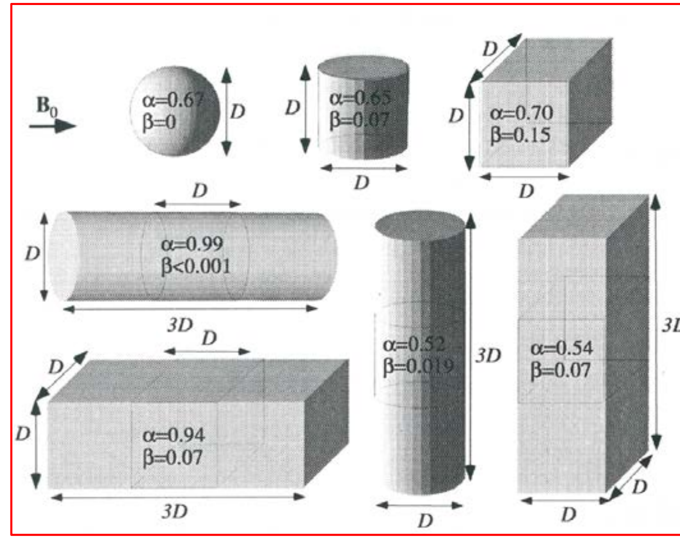
Temperature dependence:

0.1 ppm for ΔT=10 °C at 25° C in water

B.W. Petley et al., Metrologia 20, 81 (1984)
Yu I Nerenov et al., Metrologia 51, 54 (2014)

Accuracy: Susceptibility effects





$$\alpha = \frac{1}{\chi}\frac{\omega_0(\chi)-\omega_0(\chi=0)}{\omega_0(\chi=0)}$$

Material	χ (10^{-6})	Material	χ (10^{-6})
Air	+0.37	Platinum	+290
Water	-9.05	Aluminum	+20.9
Quartz	-11.8	Copper	-9.6
Teflon	-10.5	Silver	-24
FR4	-5	Gold	-34
SU8	-9.75	Silicon	-4.2

Susceptibility and **Shape** of:
- Objects in proximity to the sample
- Sample itself

Susceptibility effects: up to **10 ppm**

Accuracy: summary

Accurate "calibrations" (in given material, temperature, sample shape,...)

0.01 ppm

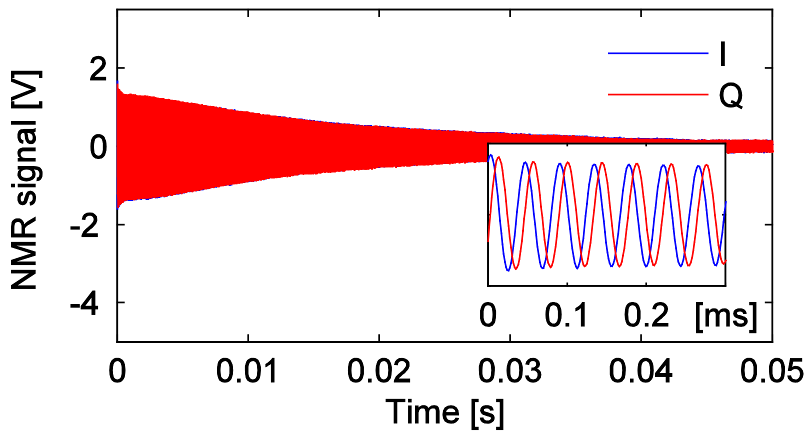
Temperature dependence:

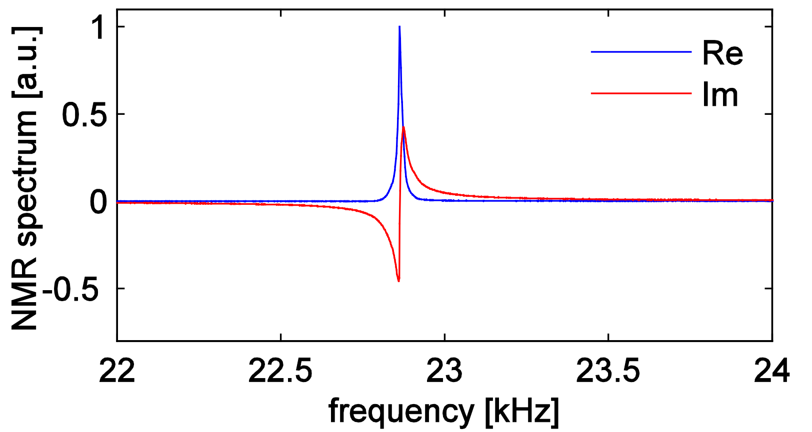
0.1 ppm for ΔT=10 °C at 25° C in water

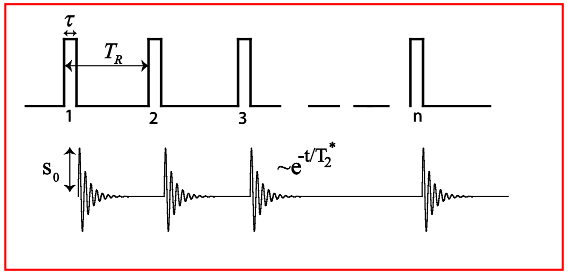
Susceptibility effects:

up to **10 ppm**

Resolution: Basics







Cramer - Rao Lower Bound (CRLB):

Standard deviation on the frequency measurement ($f_{\min}$):

$$f_{\min}\ [\mathrm{Hz}] = \left(\frac{1}{T_2^*}\right)^{3/2} \frac{\sqrt{8(1-e^{-2x})}}{(s_0/N)\,2\pi\sqrt{(1-e^{-2x})-4x^2e^{-2x}}}, \quad x \equiv \frac{T_{ACQ}}{T_2^*}$$

s_0 : signal amplitude in time domain [V]

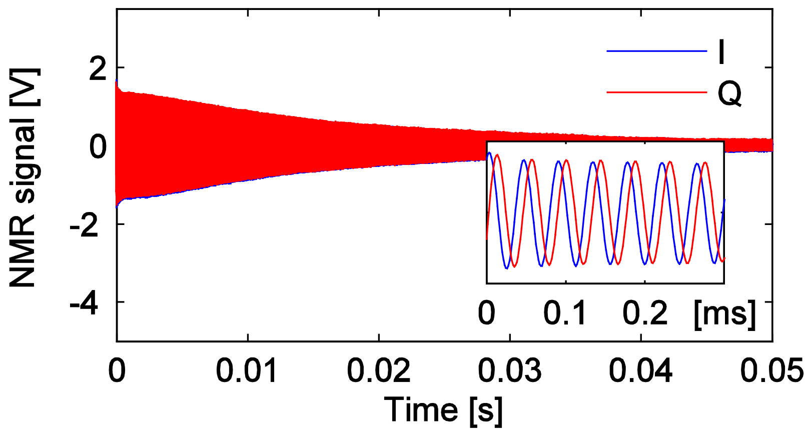
N : noise voltage spectral density [V/Hz$^{1/2}$]

T_2^* : effective exponential decay time of the signal [s]

$$f_{\min}\ [\mathrm{Hz}] \cong \left(\frac{2}{\pi T_2^*}\right)\frac{1}{s_0/N} = \frac{(\Delta f_{FWHM})^{3/2}}{s_0/N} \quad (\text{for } x \to \infty)$$

Nikiel A. , et al. "Ultrasensitive ^{3}He magnetometer for measurements of high magnetic fields." *Eur. Phys. J. D* (2014)
Gemmel C. , et al. "Ultra-sensitive magnetometry based on free precession of nuclear spins." *Eur. Phys. J. D* (2010)
Gross S. , et al. "Dynamic nuclear magnetic resonance field sensing with part-per-trillion resolution." *Nat. Comm.* (2016)

Resolution: Signal processing



«FFT»

$I(t),\ Q(t)$

$\rightarrow$

$\mathrm{FFT}\{I(t), Q(t)\}$

$\rightarrow$

Peak - finder.vi on $\mathrm{FFT}\{I(t), Q(t)\}$

(or *Lorentz fit.vi*)

$\rightarrow$

f_0

«PHASE»

$I(t),\ Q(t)$

$\rightarrow$

$\varphi = \mathrm{arctg}\left(I(t)/Q(t)\right)$

$\rightarrow$

"*Unwrap phase.vi*" on φ

and

"*Linear fit.vi*" of φ

$\rightarrow$

f_0

Resolution: Results

Probe	A	B	C	D
Frequency [MHz]	300	300	300	60
Field [T]	7.05 (SC)	7.05 (SC)	7.05 (SC)	1.4 (EM)
Sample	NR Natural Rubber	MQ Silicone Rubber	H_2O Water	NR Natural Rubber
Sample vol. [µL]	10	10	10	10
T_2 [ms]	1	1.5	3000	1
T_2^* [ms]	1	1.5	20	1
T_1 [ms]	400	600	3000	70
Chem. shift [ppm]	5.1/2.1/1.7	0	4.7	5.1/2.1/1.7
Pulse length [µs]	35	35	35	35
Repetition time [ms]	50	50	50	50
Averages	20	20	20	20
Averaging time [s]	1	1	1	1
Measurements	300	300	300	300
Measuring time [s]	300	300	300	300
s_0 [V]	1	1	1	1
N [$\mu V/Hz^{1/2}$]	8.5	8.5	8.5	8.5
Standard dev. [Hz] [nT] [ppb]	0.2 4.5 0.7	0.2 4.5 0.7	0.1 2.5 0.5	0.6 14 10
CRLB [Hz] [nT] [ppb]	0.006 0.14 0.02	0.04 0.09 0.01	0.0001 0.003 0.0004	0.006 0.14 0.1

Exp. standard deviation >> CRLB !!

Reason: Magnetic field fluctuations

(electronic noise and frequency stability of the source are negligible)

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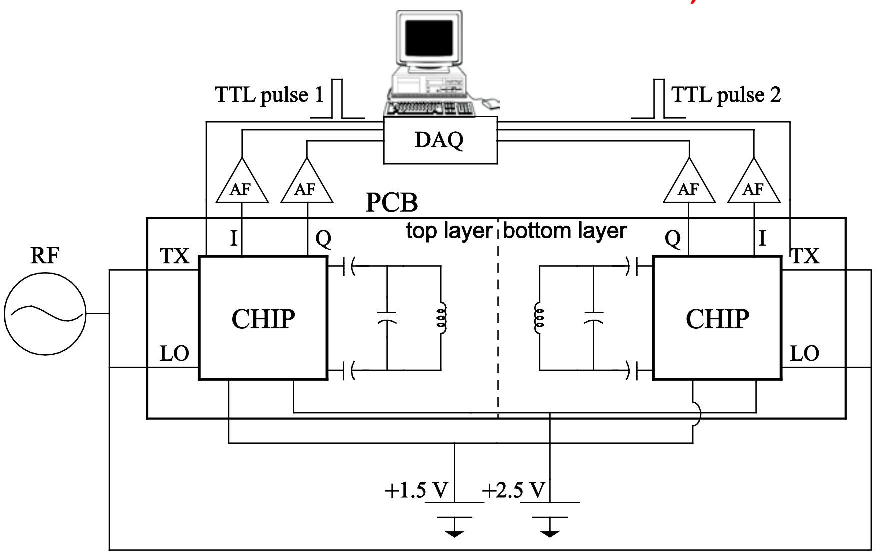
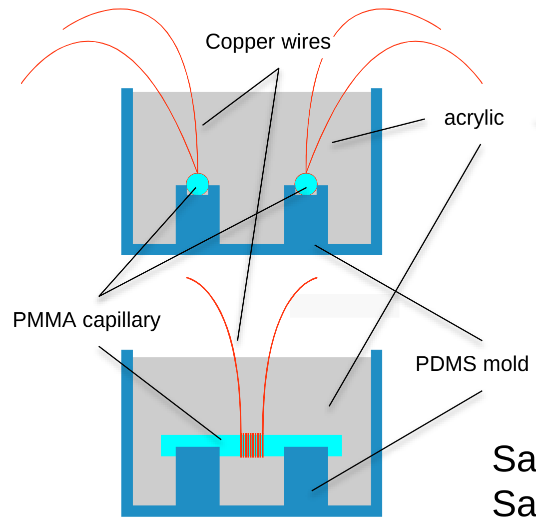
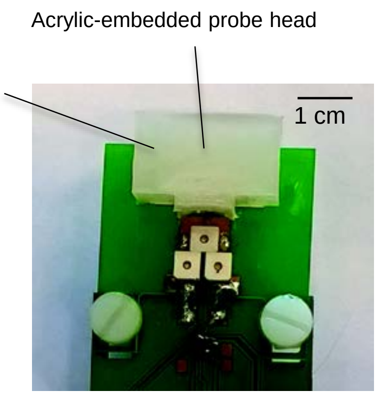
Two channels probe (to cancel field fluctuations)

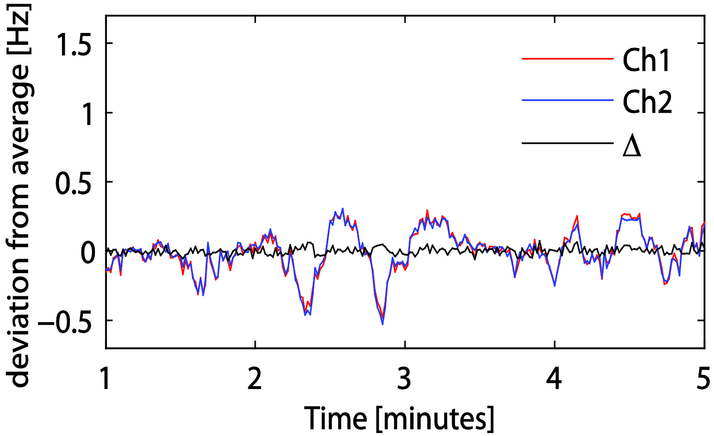
Two coils, two resonators, two single-chip IQ transceivers





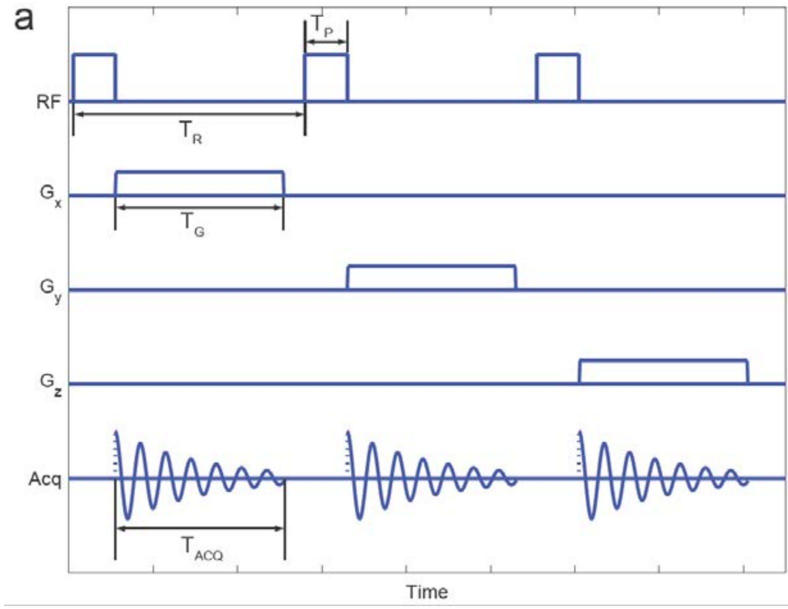


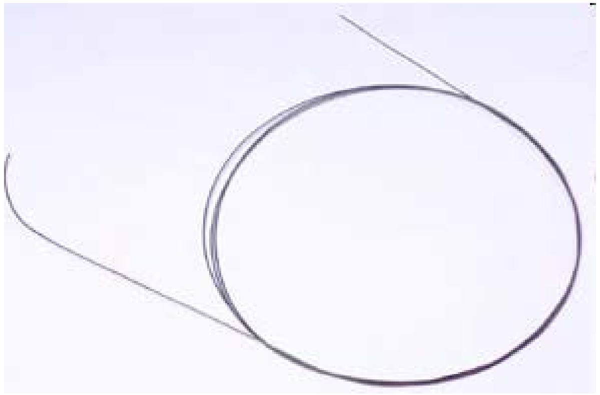
Sample material: Water
Sample volume: 500 nL

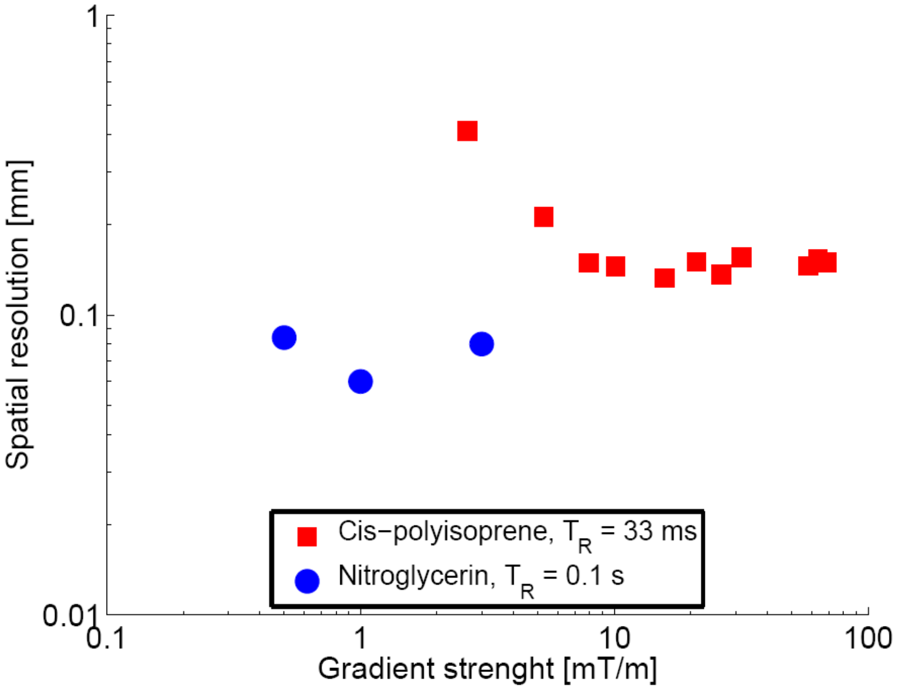


Cramer-Rao Lower Bound: 0.02 ppb/Hz$^{1/2}$
Exp. Measured: 0.06 ppb/Hz$^{1/2}$

NMR magnetometry for surgical interventions



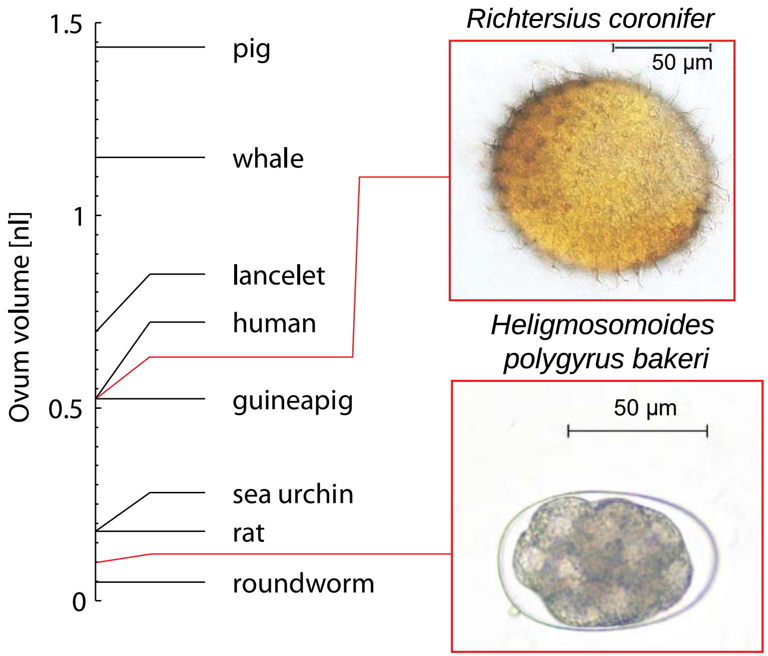


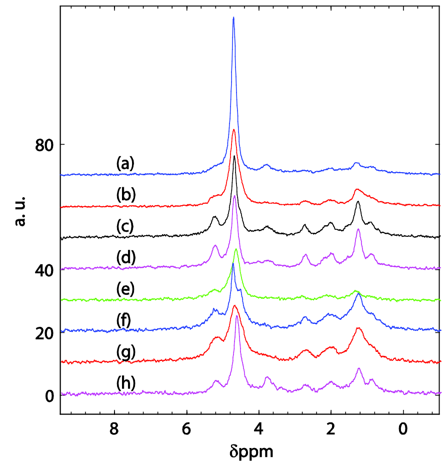


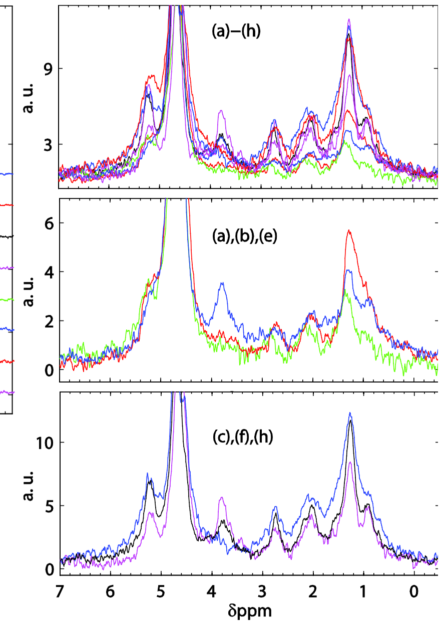
Spatial resolution: 100 μm
Time resolution: 100 ms

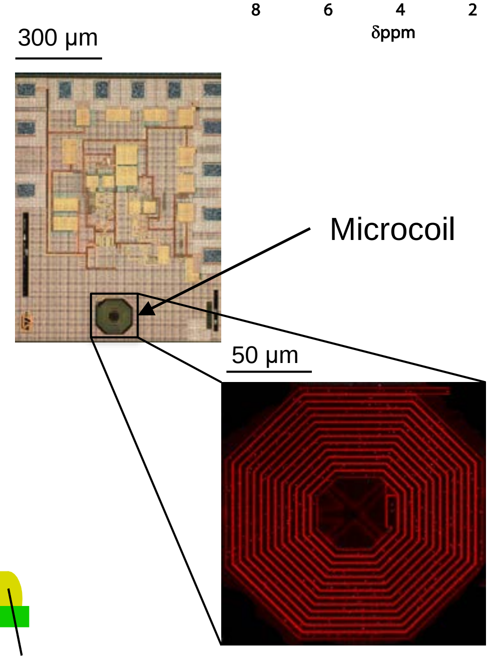
J. Anders et al., Magn. Reson. Medicine 67, 290 (2012)

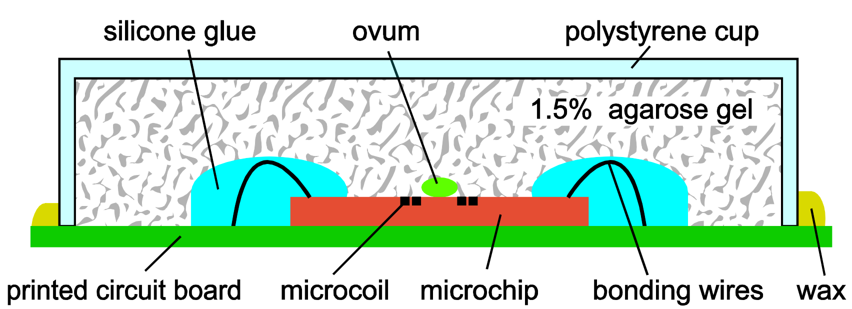
NMR spectroscopy of single sub-nanoliter eggs





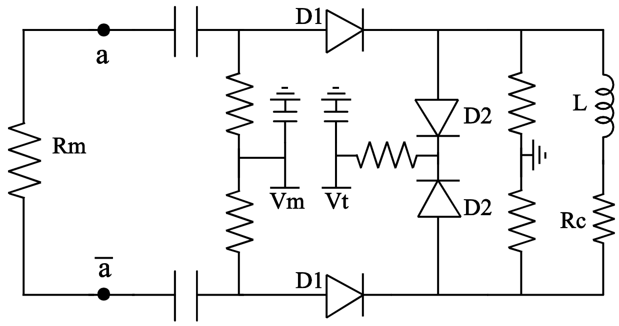






M. Grisi et al., Scientific Reports 7,44670 (2017)

Multi-nuclei excitation/detection

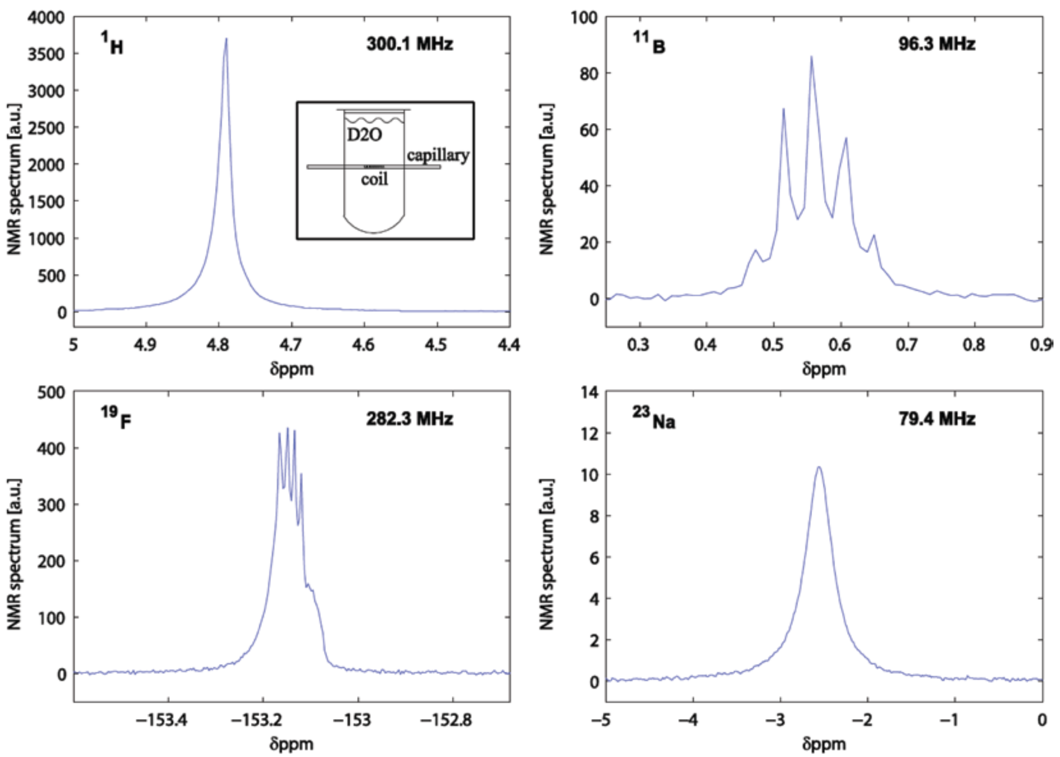


Sample

NaBF$_4$+H2O

↓

Na$^+$+BF$_4^-$ +H2O



Sponsors and people

Metrolab – Magnetic precision has a name

CTI – Start-up and entrepreneurship, R&D Funding, KTT-Support

EPFL – ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

FNSNF – SWISS NATIONAL SCIENCE FOUNDATION

Marco Grisi

Enrica Montinaro

Alessandro Matheoud

Gabriele Gualco