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A Pulse EPR 25 mT magnetometer with 10ppm resolution

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Abstract

A magnetometer designed for permanent magnet manufacturing and operated around 25 mT with 10ppm absolute accuracy is described. The magnetometer uses pulse electron paramagnetic resonance (EPR) methodology. The use of a pulsed broadband acquisition allowed reliable measurements in the presence of the magnetic field gradient and in relatively inhomogeneous magnetic fields of un-shimmed magnets.

Introduction

The modern trend in the design of the low field ($< 1.5\text{T}$) magnetic resonance spectrometers and imagers involves the use of permanent magnets. Permanent magnets are relatively simple in production and do not require power sources and magnet cooling compulsory for the electromagnets. Unlike electromagnets whose magnetic fields can be precisely calculated from the geometry of its conductors and applied currents, the fabrication of permanent magnets relies on improving the initial magnet field inhomogeneity using empirically placed compensation elements or magnet shape alterations. These procedures require precise, repetitive and spatially localized uniaxial magnetic field measurements.

Many methods have been devised for the magnetic field measurements. For high magnetic field precision and the field range from units to tenths of mT, nuclear magnetic resonance magnetometers are common. In the high field approximation, the magnetic resonance frequency is linearly proportional to the magnetic field, B_0 :

$$f = \frac{\gamma}{2\pi} B_0. \quad [1]$$

The gyromagnetic ratio, γ , depends on the nature of the magnetic particle. For water protons typically used in the nuclear magnetic resonance (NMR) magnetometers $\gamma_p = 267.513 \times 10^6$ rad/sT.

Magnetic resonance signal depends strongly on the resonance frequency.[1–3] Instruments operated at low frequencies suffer from lower signals and reduced precision of the

measurements. The majority of commercial NMR magnetometers does not work well below 40 mT or require substantial adaptation. Some of them require larger volumes of the probe heads, which reduces their spatial resolution.[3] Another drawback of NMR magnetometers is their sensitivity to magnetic field inhomogeneity. This precludes the NMR magnetic field measurement for calibration of the magnetic field gradient systems or during early permanent magnet production stages when magnetic fields are rather inhomogeneous.

Electron paramagnetic resonance (EPR) magnetometers are based on the same principal, [4, 5] however the electron $\gamma_e = 1.7608 \times 10^{11}$ rad/sT is $\gamma_e/\gamma_p=658$ times larger than that of proton leading to 658 times higher magnetometer operational frequency at the same magnetic field. As a result, better performance in the same magnetic field is expected.

For Electron Paramagnetic Resonance Imaging applications in animals, magnetic fields from 5mT (140 MHz) to 35mT (980 MHz or ~ 1 GHz) are used.[6] For fabrication of a 25 mT permanent magnet, we have designed a dedicated magnetometer.

Materials and Methods

The magnetometer scheme

Many commercial magnetic resonance magnetometers utilize continuous wave excitation and tunable resonators with the resonator frequency locked to the magnetic resonance frequency. The resonant field is determined by a frequency scan. This design is convenient for a wide range of operation. More sensitive, locking amplifier based detection is not typically used because it requires rather complex probe design with magnetic field modulation coils. For our magnetometer, we used pulse excitation with broadband pulses, which bandwidth is sufficient to cover the desired frequency range. In principle, the even broader range of operation can be achieved by adjusting the magnetometer frequency, but this was not required for our application. Pulse excitation magnetometers are common for NMR, (see e.g. [7, 8]) but to our knowledge, this scheme has not been used for EPR magnetometers.

For the EPR magnetometer bridge, we have used a homodyne scheme similar to EPR bridges published earlier.[9] The components of the magnetometer were chosen to provide cost efficient minimalistic solution (Figure 1). The reference frequency was generated by EVAL-ADF4351EB1Z (evaluation board, Analog Devices, Norwood, MA) with its loop filter frequency modified to 700 MHz. The timings of the magnetometer were controlled using Arduino UNO (<http://www.arduino.cc/>) board programmed to deliver non-interrupted 3 channel output of TTL signals for a pulse modulator (6), a transmit/receive (T/R) switch (9) and a start of acquisition signal to a Pico scope. A T/R switch was made using ZFSWA2-63DR+ SPDT switch (1W, Mini-Circuits, Brooklyn, NY) switch that switches between the resonator connection to excitation and detection arms of the spectrometer. A ZPUL-30P 100mW wide band pulse power amplifier with a rise time of 1.1 ns (8) (Mini-Circuits) was used. Due to the high EPR signal, no video amplifiers were used after the mixers (15,16). Signals were detected using 3402A digital oscilloscope (Pico Technology, Cambridgeshire, UK) which has 50 MHz bandwidth with 16 ns time resolution. The entire bridge and control elements were housed in a 19" rack-mounting case (Fig. 1C). The imager

was controlled using custom-built software written using C# (Microsoft, Redmond, WA, USA). The frequency source, Arduino UNO and Pico Scope were powered and controlled through a USB hub connected to a laptop computer running Windows 8.1 (Microsoft, Redmond, WA, USA).

Resonator

The resonator coil ($\varnothing 2.9\text{mm}$, length 2.6mm) was made with 4 turns of #20AWG copper wire (Figure 2). The resonant system was excited through a 15.5 cm balanced line using a balun (TP-101-PIN, MACOM, Lowell, MA) housed together with a matching circuit. The length of the transmission line was designed to form the equivalent of the resonant capacitor. The use of balanced transmission line allowed placing bulky tuning and matching elements remote from the tip of the probe without compromising its performance (Fig. 1B). The resonator coil was tuned to a nominal frequency of 700MHz , and the loaded quality factor of 20 is achieved using $5.6\text{K}\Omega$ shunt resistor R. The resonator had $\sim 35\text{ MHz}$ bandwidth and efficiency $\Lambda = 0.24\text{mT}/\text{W}$.

Spin probe

LiPC spin probe was purchased from the laboratory of Prof. Harold Swartz, Dartmouth Center for the Study of Viable Systems, Hanover, NH. The sample was crushed to fine powder, deoxygenated and sealed in a glass tube ($\text{ID}=1.5\text{mm}$, $\text{OD}=2.0\text{mm}$, sample weight 2.57 mg).

Operation

A 32 us long free induction decay (FID) was collected after a single 60 ns (76mW RF power) RF pulse. 8000 FIDs with a repetition time of 40us were averaged, 8-times zero-filled and Fourier transformed. The frequency corresponding to the maximum Fourier Transform intensity was determined from the fitting of the EPR line shape to a Lorentzian line profile. The FID frequency was added to the base frequency of the bridge and divided by $\gamma_e/2\pi$ to obtain the magnetic field.

The signal to noise ratio (SNR) of the field domain EPR spectrum was about 500. We have tested the stability of the readings of the magnetometer in a temperature-stabilized permanent magnet, and the readings were stable to within $0.1\text{ }\mu\text{T}$.

Table 1 summarizes the magnetometer specifications.

Discussion

Comparison to NMR magnetometers

Comparison between NMR and EPR magnetometers can be rather complex due to different designs of hardware and 6 orders of difference in relaxation times. Here we provide a crude estimation. The maximum macroscopic magnetization produced by N spins S in magnetic field B_0 is:

$$M_0 = \frac{N\gamma^2 S(S+1)}{3kT} B_0. \quad [2]$$

Here k is Boltzmann constant, and T is the temperature. The amplitude of signal induced in a resonator is proportional to signal frequency, f , and induced magnetization. Noise root mean square voltage frequency dependence is $f^{1/4}$. [2] The amplitude of the signal in the field domain is inversely proportional to spin probe line width (LW). Multiplying these factors, using [1] and ignoring differences in hardware performance between EPR and NMR magnetometers we arrive at:

$$SNR \sim \frac{N}{LW} \gamma^{11/4} \quad [3]$$

The spin probe choice

As a spin probe, we chose LiPc spin probe which has very high spin density and narrow (for EPR spin probes) line width (HWHH) of $\sim 3.5 \mu\text{T}$ at 25 mT. [10] The reported density of spin probe is $9.2 \cdot 10^{19}$ spin/g which, using an estimated density of 0.5 g/cm^3 for the spin probe powder leads to the concentration of spin probe of 76.5 mM. This concentration is 1400 times lower than the concentration of protons in water (110 M). The LiPc linewidth of 98 kHz is approximately 10^5 times broader than the linewidth of water proton. Multiplying all these factors, we obtain the LiPc/water proton signal ratio of about 1 in the homogeneous magnetic field. While SNRs of EPR and NMR magnetometers may be comparable in the homogeneous field, EPR will have higher sensitivity in a slightly inhomogeneous field. This is due to the much smaller fractional increase of EPR line width in comparison to the water proton linewidth. For example, the field inhomogeneity of $3.5 \mu\text{T}$ will decrease the NMR signal by a factor of 176, but will decrease LiPc signal only twice. This makes EPR magnetometer more versatile and better suited for permanent magnet manufacturing.

The spin probes with narrower line widths and higher concentrations will be of advantage. Particulate spin probes other than LiPc can be used as discussed elsewhere. [5] Due to the scarcity of relaxation data and the strong dependence of EPR line width on the magnetic field, it difficult to predict applicability of these probes to 25 mT. The narrow line soluble spin probe, like trityl, can also be considered. [11] The absence of powder pattern due to motional averaging of soluble probes may lead to higher magnetometer precision.

Spatial resolution

The spatial resolution of the magnetometer probe is equal to the linear dimension of the sample fraction that significantly contributes to the detected EPR signal. The RF coil has a cylindrical shape with $\varnothing 2.9 \text{ mm}$, length 2.6 mm. Taking into account the fringe fields of the coil, the spatial resolution can be estimated to be 3 mm. Considering high SNR of the method, there is no practical limitation in decreasing the spatial dimension of the probe by a factor of 3, if necessary.

Precision

Measurements of the magnetic field in a permanent magnet demonstrated the stability of the readings within 4 ppm. The precision of the measurements depends on the stability of magnetometer base frequency and digitizer time base as well as on the EPR signal and the algorithm for determination of the resonant frequency. The RF source that we used has a precision which by far exceeds the overall precision of the magnetometer and thus can be excluded from this estimation. Thus the precision is mostly governed by the EPR signal analysis and signal maximum determination. We estimate that the EPR line peak position can be found to the precision of at least $1/20^{\text{th}}$ of the EPR line width or better than 10 ppm (at 25 mT).

The absolute accuracy of the magnetometer depends on the knowledge of the spin probe gyromagnetic ratio (or g-factor). The X- and Q- band studies reported the range of LiPC g-factors from 2.0014 to 2.00226.[12–14] From these data, an absolute precision can be estimated to be ~250 ppm. However, if the gyromagnetic ratio of the spin probe can be calibrated using a magnetic field standard, much higher absolute accuracy can be achieved.

Potential applications

The magnetometer described above has been designed for the measurements of the magnetic field during construction of the permanent magnets. This application requires high precision measurements in a narrow range of magnetic fields. There are, however other applications of a magnetometer that may demand a broader range of measurable magnetic fields. The adaptation of the instrument to a broader range will include non-resonant coil or resonator with lower quality factor and the magnetometer frequency scanning. The resonator used in this work had a quality factor of 20. The power required for optimum spin excitation is inversely proportional to the resonator Q. The detected signal amplitude is proportional to the square root of Q. Making the coil non-resonant will decrease instrument signal-to-noise ratio by a factor of 4.5 and may increase acquisition time by a factor of 20. Another problem that has to be solved is the limited bandwidth of the excitation pulses. The direct increase of pulse bandwidth can be accomplished by the use of shorter pulses. This will increase the necessary radiofrequency power. An alternative solution will be to use multiple magnetometer frequencies. The operation range can be broken into multiple subranges, and the central magnetometer frequency can be switched between these ranges. The magnetometer operated in a broad range of fields should be built using broadband components or use multiple channels for different frequencies.

Conclusion

We presented a simple, low-cost magnetometer for use in the low to intermediate magnetic field range. High precision and insensitivity to inhomogeneous fields make this magnetometer well suited for permanent magnet manufacturing.

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Figure 1.

A. Scheme of the magnetometer bridge. (1) RF source, Analog Devices EVAL-ADF4351EB1Z; (2) Band pass filter, Mini-Circuits VBFZ-180-S+; (3, 14) 3dB splitter, Mini-Circuits ZX10Q-2-13-S+; (4, 19) LNA, gain 24dB, Mini-Circuits ZX60-P103LN+; (5,18) Variable attenuator, ALAN 50CA1-15; (6) Switch, Mini-Circuits ZASWA-2-50DR; (7, 12) Low pass filter, Mini-Circuits SHP-400+; (8) Pulse amplifier, Mini-Circuits ZPUL-30P; (9) Mini-Circuits ZFSWA2-63DR+; (10) 2W limiter, Mini-circuits VLM-63-2W+; (11,13) LNA, Advance Receiver Research P700VDG; (15,16) Mixer, Mini-Circuits ZLW-2; (17) 90° 3dB splitter, Mini-circuits; ZX10Q-2-13-S+. B. Magnetometer probe with the exposed RF coil. C. Magnetometer with the control computer.

Figure 2.
Electric scheme of the magnetometer probe.

Table 1

The summary of the magnetometer specifications

Magnetic field range	25 mT +/- 1mT
Precision	< 10 ppm
Active area	3mm × 3mm × 3mm
Measurement time	0.5 s
Maximum field gradient *	10 mT/m

* Maximum gradient of the magnetic field in which reliable measurements of the magnetic field are possible