SQUID based LF-NMR measurements in an urban laboratory environment

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Abstract. Nuclear magnetic resonance measurements were performed in an urban laboratory environment using a second-order low-Tc superconducting quantum interference device (SQUID) gradiometer. A static-active combined compensation system, consisting of three pairs of $2 \times 2$ m$^2$ orthogonal squared Helmholtz coils, a 3 axis fluxgate, and home-made feedback electronics were constructed, and the low frequency variation of the environment was reduced by more than one order of magnitude; And its application in LF-NMR measurement was also discussed. A simple but efficient pre-polarization ($B_p$) coil was fabricated, and $B_p$ exceeding 100 mT was achieved. NMR signals of proton were studied in both time and frequency domain, during both midnight and daytime. In the case of daytime measurement, the authors suggest the use of selective average, which can partly overcome the disadvantage of fluctuations of the ambient magnetic field.

1. Introduction

In recent years there has been increasing interest in nuclear magnetic resonance (NMR) performed at low measurement field ($B_M$) strength in the range below 1 mT. The growth of interest in this field can be attributed to the wide range of potential applications for portable and/or ex situ NMR and MRI systems. The innate limitation of low-field (LF) NMR is its low signal-to-noise ratio (SNR). To partially overcome this limitation, researchers can use a Superconducting Quantum Interference Devices(SQUID) as the detector. This is an ideal candidate for the NMR detector, because of its unequalled sensitivity and broad bandwidth, especially in the low frequency [1-3]. For a general review of SQUID-based NMR research one can refer to Greenberg’s article [4]. The UC Berkeley’s group recorded NMR signals with Larmor frequencies $f_L$ from several tens of Hz to MHz utilizing nitrogen-cooled (HTS) or helium-cooled (LTS) SQUIDs [5-7]. Burghoff et al. reported NMR spectra of distilled water with a resolution well below 1 Hz at ultra-low fields of 40 nT to 4 µT [8]. Meanwhile, we performed some LF-NMR measurements using a HTS radio frequency (rf) SQUID [9].

In SQUID-based LF NMR, the $B_M$ is often comparable to the Earth’s magnetic field (EMF, around 30–50 μT) or smaller, the spatial and time domain fluctuations of the environmental field thus become the major challenges to overcome, especially in an urban environment, where the EMF is highly distorted by buildings, and contaminated by transportation, power lines, electrical appliances, etc. The challenges have been dealt with in different ways. Most of the researchers put their

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experiment set-ups in magnetically shielded rooms (MSR), which was highly efficient but costly and inconvenient [8–10]. The Berkeley group built two or three orthogonal pairs of coils to cancel the Earth’s magnetic field. They also constructed an eddy-current shield to suppress the environmental noises in the measurement frequency band [11, 12]. During our work in the research center at Juelich, Germany, we demonstrated a high quality signal utilizing the Earth’s magnetic field as the measurement field by setting up the system in a forest far away from buildings to reduce the fluctuation and inhomogeneity of EMF [13].

In this work, we constructed a SQUID based LF-NMR system in an urban laboratory magnetic environment. Firstly, the homogeneity and fluctuation of environmental magnetic fields were investigated; a static-active combined compensation system was constructed, and its application in LF-NMR measurements was discussed. The time and frequency domain LF-NMR signals were recorded both during midnight and daytime. In daytime measurement, a selective average method was applied to partially overcome the fluctuation of environmental magnetic fields.

2. Experimental Setup

Our ULF-NMR experiments were performed in a 5th floor laboratory. Three pairs of 2×2 m² orthogonal squared Helmholtz coils were located in the center of the laboratory. The coil system was oriented so that one pair is along the horizontal component of EMF. A low-Tc hand-wound second-order axial gradiometer was used as the NMR signal detector, (see [14] for details). The SQUID system was positioned at the bottom of a fiberglass cryostat filled with liquid helium. The liquid sample (tap water, ~ 10 ml) was located beneath the bottom of the cryostat finger (see Figure 1 (a)). The distance between the sample center and SQUID was estimated to be 32 mm. The Earth’s magnetic field was used as the measurement field ($B_m$), with its vertical component being compensated by the corresponding square Helmholtz coil pair. The $B_m$ was determined to be ~ 29.8 $\mu$T, corresponding to the proton Larmor frequency $f_L \sim 1270$ Hz. An 8-layer squared solenoid surrounding the sample was used to generate a pulsed polarization field ($B_p$), which takes two typical values of 10 mT and 100 mT. The configuration of $B_p \perp B_m$ was chosen.

![Figure 1. Measurement arrangement and pulse sequence. (a) Orientation of the SQUID system, compensation coils and the sample; (b) the pulse sequence of the measurement. The sequence was controlled by a laptop, and the recorded signal can be averaged to improve SNR.](image)

Each measurement started by polarizing the sample in a field of $B_p = 10 \sim 100$ mT for $t_1 = 4$ s (see figure 1 (b)). After $B_p$ was switched off, the sample was left in $B_m$. The SQUID readout electronics was kept in the reset state during the polarizing time $t_1$ and the following delay time of 2 ms ($\Delta t$) after
switching off $B_p$. Subsequently, the SQUID was locked to record the magnetic signal generated by the precession of nuclear magnetization for a preprogrammed measuring time $t_2$. The frequency spectra of the signal recorded by SQUID during $t_2$ were obtained by Fourier transformation using a Dynamic Signal Analyzer (LDS, Photon II). In order to clearly record the free induction decay (FID) signal in real time, the proton Larmor frequency was reduced using a mixer. A home-made multiplier was used to mix the output of the SQUID having the proton Larmor frequency of $f_L \approx 1270$ Hz with a synchronous sinusoidal wave. The signal of around 75 Hz from the multiplier output was recorded by the dynamic signal analyzer after filtering.

3. Results and Discussion

3.1 EMF fluctuation and compensation

Our experiment started with investigating the magnetic field properties of the environment, including its homogeneity and stability.

To demonstrate the spatial fluctuation of the ambient magnetic field, we recorded the magnetic field of $6 \times 6 \times 6$ points using a 3 axis fluxgate (Bartington, Mag-03MSL70); the distance between the adjacent points is 40 cm. For each point, 3 components were recorded for 10 s, and the mean value was taken to be the magnetic field. In the regime around the sample, the field gradient of $4 \sim 6$ nT/cm was measured.

The time domain fluctuation was also investigated using the same fluxgate. The fluxgate was put in the center of the lab, and the 3 components were recorded for 24 hours (frequency band: 10 Hz). Figure 2 (a) shows the vertical component from 8:00 PM to the next 8:00 AM. There are obviously two periods: during the midnight (lasts for about 4 hours, from 0:30 AM to 4:30 AM), the field fluctuation is in the order of nT; out of this period, the fluctuation increased dramatically, and varies over 1 µT. Two horizontal components take the same shape as Figure 2(a), but have one order of magnitude smaller amplitude, or say, vary within $\pm 50$ nT.

![Figure 2](image)

Figure 2. (a) The vertical component of EMF recorded by a fluxgate within 12 hours. (b) Three perpendicular component of EMF when static compensation were applied, Curve (I) and (II) are the horizontal component and curve (III) represents the vertical component. (c) Three perpendicular component of EMF when static-active compensation was applied. The measurements in (b) and (c) were made during the noisy day.

To reduce the low frequency time domain fluctuation, three pairs of $2 \times 2$ m$^2$ orthogonal squared Helmholtz coil formers were constructed. In each coil former, two sets of independent coils were wound. One set for the static compensation (winding No.: $N_1 = 30$) and the other for active compensation (winding No.: $N_2 = 10$). One can tell from Figure 2 (b) that, the static compensation can reduce the amplitude of the field, but without suppressing the fluctuations.

In addition to the static compensation, active shielding was realized by home-made feedback electronics, which contain three independent sets of pre-amplifier, integrator and power-amplifier, and the offset and bandwidth of which can be adjusted manually. The fluxgate was put in the center (or a
certain distance away from it), and the recorded signal were fed to the electronics, which then drive the active compensation coils to generate an opposite compensation field. Figure 2 (c) shows the static-active combined shielding field. We can see that the fluctuation was suppressed within ±10 nT in vertical direction (curve III) and ±5 nT in horizontal directions (curve I and II). Compare Figure 2 (b) and (c), we can say that the static variation of the environmental magnetic field was reduced by more than one order of magnitude.

3.2 real time signal and spectra of water
The innate limitation of low-field (LF) NMR is its low signal-to-noise ratio (SNR). To partially remove this limitation, a pulsed $B_p$ was applied. The $B_p$ coil former was made of 4 pieces of AlN substrate, which has outstanding Thermal conductivity. The 760-turn coil has a resistance of $R = 4.2 \Omega$ at room temperature, and the magnetic field was measured to be 10.5 mT/A in the center of the coil. A $B_p$ of 100 mT can be achieved readily with such a coil.

Figure 3(a) shows four single shot spectra of 10 ml tap water under different $B_p$. It is obvious that the SNR increase linearly with $B_p$. But even in the case of $B_p = 100$ mT, the SNR is around 25.

The relatively low SNR is mainly due to the inhomogeneity of the environment, or say, the relative broad linewidth. In our previous work [9], the natural linewidth of 0.123 Hz was measured for water sample, but the linewidth in Figure 3(a) were broadened to be around 4 Hz. This broadening reduces the amplitude of the peak, and the SNR of the measurement [15].

The broadened linewidth indicates a shorter transverse relaxation time ($T_2^*$), so we can reduce the measurement time reasonably. Figure 3 (b) shows the homologous spectrum of curve (IV) in Figure 3 (a), but the measurement time was reduced from 0.8 s to 0.4 s. One can tell that the SNR increased obviously. In fact, it reaches 38 for single shot.

Another method to further improve the SNR in NMR is the averaging of repetitive measurements. Providing that the experimental conditions were stable and that the noise was white and Gaussian, the SNR should increase with the square root of the number of averages. According to Figure 2(a), the field fluctuation reduces dramatically during midnight, so we first averaged our measurement during midnight.

Figure 4 (a) shows a 50-times averaged FID signal recorded around 1:30 AM. At the same time, every frame of the spectra was investigated. The peak frequency was counted and distributed in the insert of Figure 4 (a). One can find that, after 50 times average, a relative high SNR was obtained. And the mixed frequency was located at 73.75 Hz stably.
As a contrast, the averaged measurement was carried out during a “noisy” time (around 8:00 PM), and the results are illustrated in Figure 4 (b). As one can notice, the 50-time averaged FID still has an acceptable signal. The main difference is its more decentralized frequency distribution. Just as the insert shows, only 40% of the spectra have the same Larmor frequency. This influences the phase coherency of each frame; and thus damages the property of the averaged signal in a certain degree.

![Figure 4](image) FID signals detected during midnight (a) and daytime (b). The insert in each graph indicates the frequency distribution of its corresponding spectrum. $B_p = 10$ mT, $t_1 = 4$ s, average times: 50.

Since the dispersed peak frequency would influence the property of the averaged signals, one can avoid this artifact by selecting the frames with the center frequency and carrying out the average process offline. Figure 5 shows such an averaged FID signal. In this case, 20 frames with peak frequency of 71.25 Hz were selected (see the insert in Figure 4 (b)). Compared with Figure 4(b), the 20-time selective averaged FID signal in Figure 5 has even better property (both the amplitude and $T_2^*$). This selective average encourages one that it is possible to obtain some satisfactory results in a relative noisy magnetic environment.

![Figure 5](image) FID signal after selective average. $B_p = 10$ mT, $t_1 = 4$ s, average times: 20.

### 3.3 active-shielding aided LF-NMR measurements
The previous investigations in 3.2 were performed without active shielding. Here we discuss some LF-NMR measurements when active-shielding was applied.

For active-shielding in 3.1, the fluxgate was put in the center of the coil set. However, when the LF-NMR measurement was performed, the liquid sample and SQUID system should be located in the center; and the fluxgate should be put some distance away from them, in order to reduce the influence on SQUID and field homogeneity. During the measurement, the fluxgate was put 40 cm away from the center, and the orientation was adjusted carefully so that the influence of \(B_p\) switching can be minimized.

Figure 6 (a) illustrates a 50-time averaged FID signal when the active-shielding was applied. One can say that the time average also works in this case. But the signal within the first 50 ms was destroyed.

During our LF-NMR measurement, a pulsed \(B_p\) is needed, and the switch of \(B_p\) can cause a pulsed field in the feedback fluxgate, though its orientation is carefully adjusted. Figure 6 (b) and its insert show the vertical component when active shielding was applied. We can notice that, after \(B_p\) was switched on/off, a sharp pulse will generated in the fluxgate and hence the feedback system. The width of the pulse is around 50 ms, which agrees with the destroyed time in Figure 6 (a).

![Figure 6](image)

**Figure 6.** (a) FID signal of 10 ml tap water when active shielding was applied. \((B_p = 10 \text{ mT}, t_1 = 4 \text{ s}, \text{average times: 50})\). (b) Active shielded magnetic field recorded by a fluxgate (as a typical case, just the vertical component was shown).

### 4. Conclusion and Outlook

Under the Earth’s magnetic field in an unshielded urban laboratory environment, nuclear magnetic resonance signals of water were detected utilizing a second-order SQUID gradiometer. A 3-dimensional static-active compensation system was demonstrated to reduce the fluctuation, satisfactory results were obtained. However, due to the pulsed \(B_p\) in LF-NMR measurement, the virtue of active compensation was restricted. The measurements during midnight and daytime were performed. In both cases, time-averaging works, and in the later case, a method of selective averaging was suggested, which can partially avoid the artifact caused by the fluctuation of field.

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