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Efficient compensation of low-frequency magnetic field disturbances in NMR with fluxgate sensors

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Abstract

A simple stabilization scheme of B_0 magnetic field fluctuations is described. The method is based on external measurements of time dependent magnetic field fluctuations by fluxgate sensors and generation of a compensating correction current in a coil mounted directly on an NMR magnet. It is shown that such an approach efficiently eliminates relatively slow magnetic field variations with frequency up to approximately 100 Hz. In combination with a standard ^{2}H field-frequency lock system, the method enables acquisition of reproducible lineshapes and dramatically improves overall performance of a high resolution NMR spectrometer. The presented solution might substitute for the internal lock system in these case where deuterium lock is not available.

Keywords: Compensation of magnetic field disturbances; Fluxgate sensors; Field-frequency lock; Correlation spectroscopy; ^{2}H NMR

1. Introduction

Environmental stability of high resolution spectrometers is crucial for their intrinsic performance and sensitivity [1–4]. The most common causes of spectrometer instability are variations of room temperature, mechanical vibrations, and fluctuations of external magnetic field. In the urban areas, the motion of massive ferromagnetic objects, such as elevators, and fluctuating DC power lines are major sources of magnetic field noise. The noise originating from DC power supply lines of the city transport system is especially difficult to avoid for NMR facilities located in downtown areas. The Chemistry Department of Warsaw University is located in the vicinity of such power supply lines. This results in approximately ±10 Hz fluctuations of the ^{1}H resonance frequency as observed without the ^{2}H lock (Fig. 1A). A relatively small amplitude of frequency fluctuation during night time indicates that the city public transport is the source of the noise. At the location neighboring of the NMR spectrometer, a fluxgate-type [5,6] magnetometer sensor shows fluctuations of the magnetic field with amplitude of approximately ±3 μT and the field change rate of up to ±25 μT/s (Fig. 1B). Under these conditions, the standard ^{2}H lock system is unable to fully compensate for external disturbances. This results in an increased noise (especially the "t_1 noise" in 2D experiments), irreproducible lineshapes, and significant difficulties in all experiments that require long term stability.

The standard way to stabilize the B_0 field inside the NMR sample is the deuterium field-frequency lock. The most important advantages of this solution is a high precision of field stabilization and the fact that the correction signal is generated in the sample volume. However, the lock feedback loop is based on measurements of very small frequency change (note that $\gamma(^2\text{H})$ is approximately 6.5 times lower than $\gamma(^1\text{H})$). Since the precision of the frequency determination is inversely proportional to the measurement time, precise B_0 stabil-

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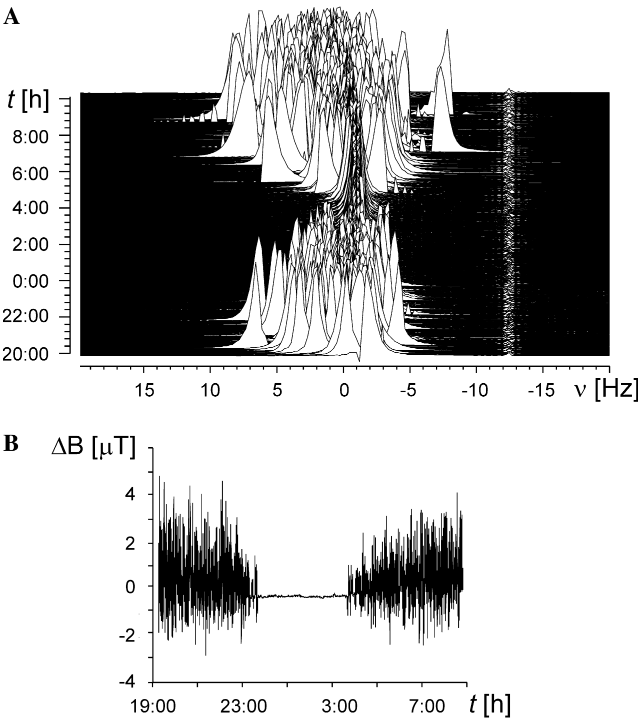

Fig. 1. Time dependence of magnetic field fluctuations as observed by relative shifts of the Larmor frequency (A), and measured by the magnetometer (B). The stack-plot shown in (A) was obtained by acquisition of $CHCl_3$ ^1H signal every 1 min using standard sample of 1% $CHCl_3$ in acetone-d_6.

ization is possible only for relatively slow field changes. Thus the usual lock time constants in common spectrometers are of the order of tens of seconds. On the other hand, the conventional approach to eliminate high frequency field fluctuations is to use a passive shielding by ferromagnetic plates. However, this method is difficult and inefficient when the field fluctuates slowly.

Although the newest generation of cryomagnets is less sensitive to external magnetic field instabilities, a simple and inexpensive solution proposed in this paper to correct the B_0 field instability could be still useful for older systems, or for spectrometers located in noisy areas. In addition, external B_0 field stabilization could be used for substituting the field-frequency lock in those applications where the ^2H lock cannot be used.

2. Results and discussion

The general concept of compensation of the magnetic field fluctuations is based on an external field measurement resulting in an input error signal. This signal is used to generate a correction current in a coil mounted on the NMR cryomagnet dewar. For the input error signal measured in direction parallel to the magnet B_0 axis, we assumed that the time dependence of the field variations is spatially independent. This assumption is true in the first approximation, if location of the source of instabilities is known and the source is much stronger than background electromagnetic noise. This is the case when the distance to the source of instabilities is relatively short.

2.1. Description of the compensation device

From the variety of available magnetic field sensors, we selected a fluxgate sensor [5,6] as the most suitable for this application. Commercially available fluxgate sensors are low-cost vector devices, capable of high precision 1 nT magnetic field measurement. The output signal from the fluxgate sensor is easily converted into digital form since it has the form of rectangular pulses with period directly proportional to the field strength. Using of digital signal received from the sensor enables easy computer or microcontroller analysis of error signal and calculating of adequate correction. Additionally, computer control makes achievable adjusting of correction parameters to specific features of disturbance character like for example programmed changing of compensation range and rate with depending on the conditions change, i.e., in 24 h cycle. Moreover, it is possible to record field fluctuations with adjustable rate. For the NMR measurements without use of field-frequency lock, the digital signal processing enables simple correction for magnet drift.

There are commercially available fluxgate-driven magnetic field compensation devices as for example MR-3 by Stefan Mayer Instruments (www.stefan-mayer.com). However, this is analog apparatus, which limits its applicability by disabling programmable adjusting of parameters. It requires placing of sensor near to the center of compensated area, and thus it is not suitable to correction of disturbances in NMR systems, where the sensor would be saturated by high field magnet.

The schematic diagram of the compensation device is shown in Fig. 2. The FGM-3h sensors purchased from Speake & Co. Llanfapley (www.speakesensors.co.uk) produce 0–5 V rectangular pulses at the output, with $B = 0$ period of approximately 16 μs and, according to specifications, change of period by 1 μs is equivalent to field shift of 3 μT. The sensor output signal is fed into the input line of the parallel LPT port of a PC and sampled to count pulses for a preset measurement time. The calculated period is normalized to a 8-bit number (0–255) and sent back to the LPT port. The digital signal from the PC is used as an input for a 8-bit digital–analog converter which converts it to 0–2.55 V analog output. The resulting potential is amplified and converted into the compensating current that is fed through the correction coil wound directly on the NMR magnet. The described single axis construction might be easily expanded to three axis operation,

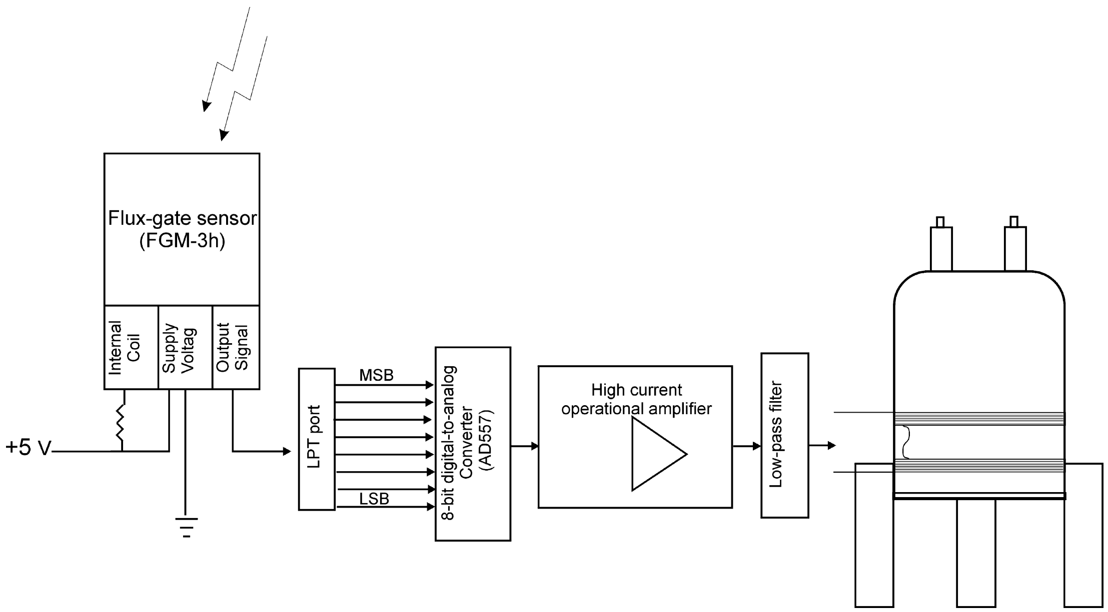

Fig. 2. The block scheme of the field compensation unit.

simply by adding of additional sensors and compensation circuits.

Calibration of the amplitude of correction signal was performed by adjusting the resistance of the correction circuit against the standard deviation of the signal position in the ^{1}H NMR spectrum acquired without the ^{2}H lock. As expected, the amplitude of the correction signal was inversely proportional to the overall resistance of the circuit, and the calibration was achieved by linear regression. In our case, the adjusted amplitude of the correction current in the coil varied up to ca. ±10 mA. The linear response of the FGM-3h sensors is approximately of ±15 μT; thus, these sensors cannot operate in the vicinity of the NMR magnet. Therefore, the fluxgate sensors were mounted away from the magnet, and the field offset of each sensor was precisely adjusted to zero using built in correction coil to ensure linear response. We have checked several locations (up to 25 m away from the magnet) and we did not find significant differences in the compensation efficiency. The correction rate (i.e., a reciprocal of the time length of the loop counting pulses generated by the sensors) was optimized with respect to the ability of compensation of fast field changes and the precision of the field measurement (which is inversely proportional to the correction rate). To increase precision, we used two identical sensors, averaging the measured periods of the fluxgate sensors. We have found that the fastest correction rate without significantly reduced precision corresponded to the measurement time of 5 ms. Further increase of the correction rate did not improve the compensation of the magnetic field noise.

2.2. NMR experiments

The sample sets of spectra acquired without and with external correction are shown in Fig. 3. These spectra were acquired without the deuterium lock. Fig. 3 shows

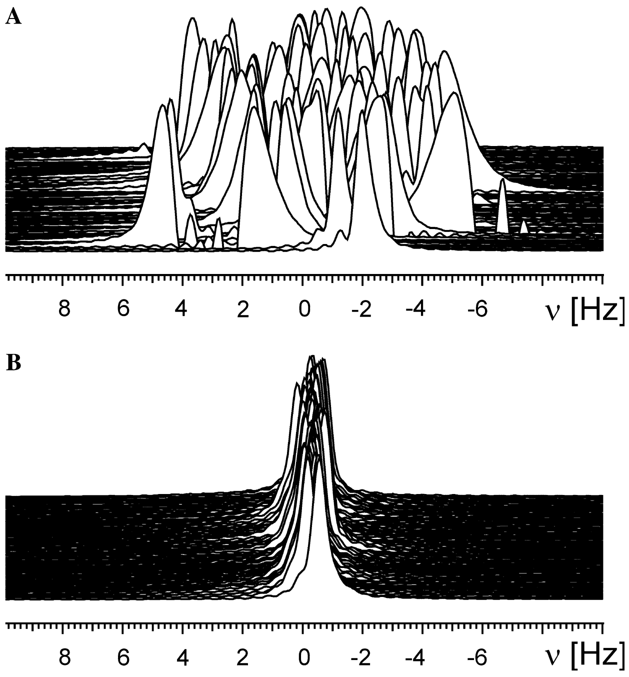

Fig. 3. Comparison of stack plots obtained by acquisition of 60 successive acquisitions of $CHCl_3$ ^{1}H signal every 1 min using standard sample of 1% $CHCl_3$ in acetone-d_6. Spectra were acquired without the ^{2}H lock: (A) without the external B_0 correction, (B) with the external B_0 correction. Acquisition parameters: the acquisition time 2 s, the spectral width 2000 Hz.

that external compensation reduces the amplitude of the signal frequency shifts by approximately one order of magnitude. The most important improvement is achieved when the deuterium lock and the external compensation are used simultaneously. Fig. 4 shows series of superimposed spectra of 1% $CHCl_3$ in acetone-d_6 acquired with the deuterium lock. It is clear (Fig. 4A) that the signal shapes are not reproducible, even with the lock system that almost completely eliminates the frequency fluctuations. The external compensation significantly reduces lineshape instabilities (Fig. 4B). This stabilization of the signal lineshape is crucial in correlation spectroscopy and/or in experiments requiring phase cycling. The practical impact of the external field compensation was tested on ^1H–^{13}C HSQC spectrum of sucrose. As shown in Fig. 5, the additional correction significantly reduces t_1-noise, increasing signal-to-noise ratio almost 10-fold. Other possible application for the external field correction is substitution of the ^2H lock when it is not available or in the case of ^2H NMR experiments. Fig. 6 shows the comparison of ^2H spectra of neat ethanol. Even though the effect of field instabilities is ca. 6.5 times weaker when observed on ^2H resonance frequencies, the effect of field correction is clearly visible. The signals in the spectrum (b), obtained with external correction, are almost two times narrower, and S/N ratio increased appropriately. Note that for longer measurements of this type the magnet drift should be evaluated and added to the correction.

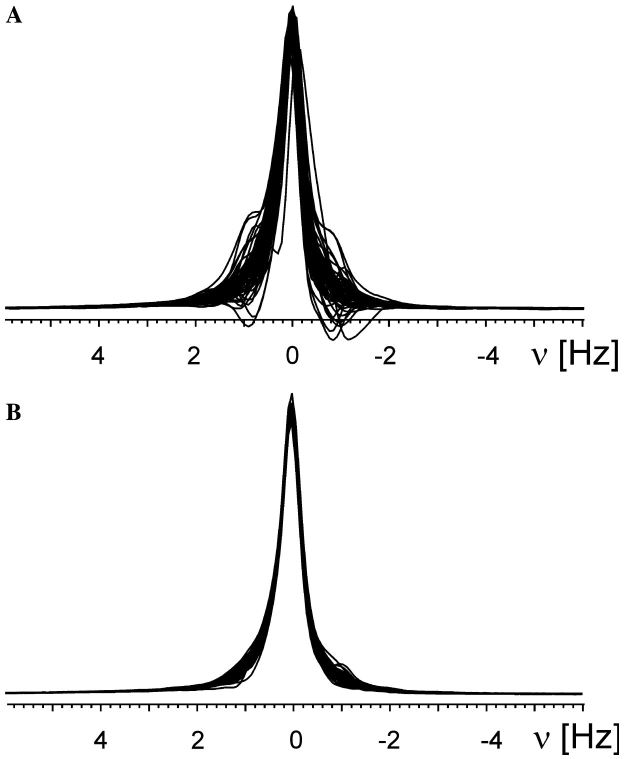

Fig. 4. The lineshape reproducibility test with the ^2H lock. (A) Without the external B_0 correction, (B) with the external B_0 correction. In both cases, 60 successive acquisitions of $CHCl_3$ ^1H signal every 1 min using standard sample of 1% $CHCl_3$ in acetone-d_6 is shown. Acquisition time of 5 s and spectral width of 2000 Hz were used.

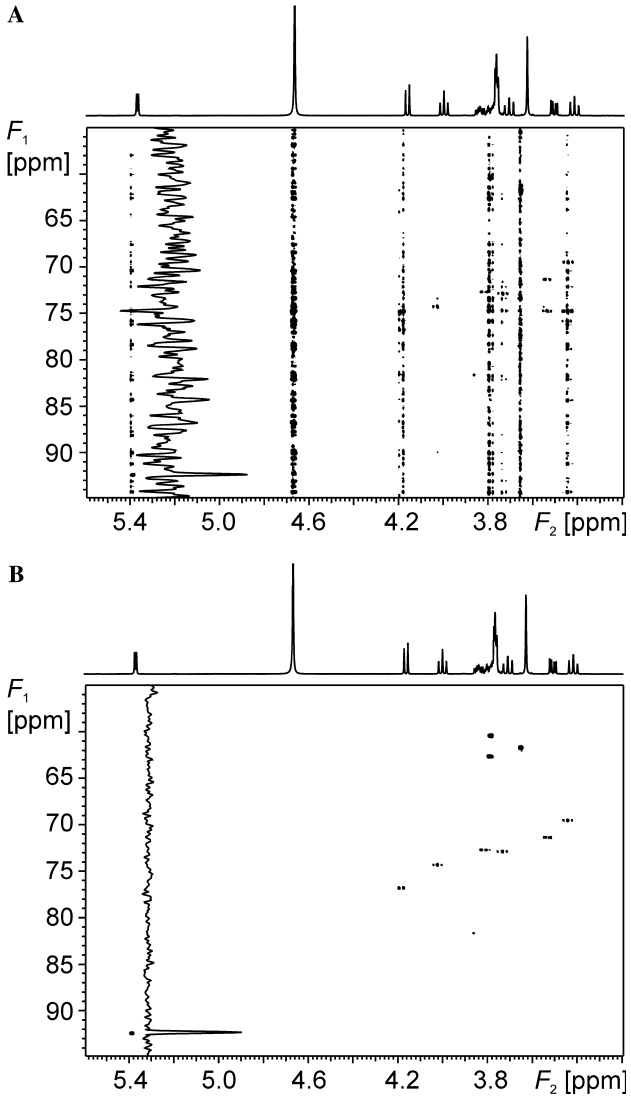

Fig. 5. The contour plots of ^1H–^{13}C–$\{^{13}C\}$ HSQC spectra of 20 mM sucrose in D_2O sample, without (A) and with (B) the external B_0 correction. The F_1 trace across anomeric proton signal is shown for evaluation of the signal-to-noise ratio. Two scans were coherently added for each data set for 256 t_1 increments. The maximum t_1 and t_2 times were 34.1 and 300 ms, respectively. A relaxation delay of 2 s was used. The data matrix containing 256 × 480 complex points in t_1 and t_2, respectively, was zero-filled to 1024 × 1024 complex points. Cosine weighting function was applied in both dimensions prior to the Fourier transformation.

3. Experimental

The fluxgate sensors FGM-3h were purchased from Speake and Co. Llanfapley (www.speakesensors.co.uk). All other materials are widely available as standard electronic parts. The correction coil consisted of two 60-turn

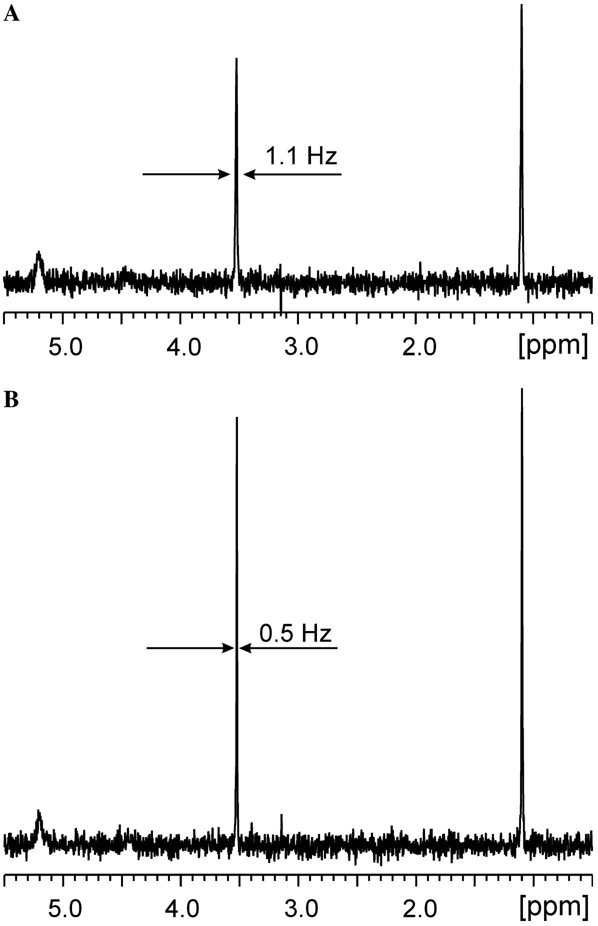

Fig. 6. Comparison of ^2H spectra acquired without lock, and without (A) and with (B) the external B_0 correction, respectively, using sample of neat ethanol in 300 K. Thousand twenty-four scans were accumulated with spectral width of 780 Hz and acquisition time of 2 s. ^1H decoupling was applied to obtain narrow spectral lines.

segments mounted in the Helmholtz configuration. Each segment was made from 60-pin flat computer cable connected in such a way that the closed loop from between first and last pin was formed. We used a 120 MHz Pentium PC under Linux Red Hat 5.1 for processing of the sensor signal and generation of the correction output. Additional information and C++ program codes are available from authors. All the spectra presented were recorded at 300 K on a Varian Unity Plus 500 MHz spectrometer using a standard 5 mm ^1H, $\{^{31}P–^{15}N\}$ ID-PFG probehead. The ^2H pulses were applied to the lock coil.

4. Conclusions

We have tested a simple and cost effective solution to the problem of external magnetic field fluctuations interfering with the B_0 field in the sample. We did not modify or change the spectrometer hardware. The construction is supplementary to the ^2H field-frequency lock, but it also could be used as a stand-alone application in such experiments as acquisition of ^2H NMR spectra, high resolution solid state experiments, and micro imaging applications. The compensation quality could be further improved by zeroing time dependent B_0 gradients and by optimization of sensor locations. Additionally, using fluxgate sensors operating at higher frequencies would allow to increase the rate of the sampling. We believe that the presented solution is simple and convenient, and could improve the performance of the NMR spectrometers located in large urban areas. The same compensation system in single to three axis configuration could be adapted to improve functionality of other devices requiring high stability of magnetic field as for example MRI scanners, electron microscopes or mass spectrometers.

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