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NMR Techniques

Small Magnets for Portable NMR Spectrometers**

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High-resolution nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. The study of large molecules such as proteins requires high sensitivity and high spectral resolution, which are both achieved with strong magnetic fields. These fields are generated by huge superconducting magnets, which are made stronger and bigger each year to tackle larger and larger molecules. The results of this amazing technological effort are bulky and static magnets permanently installed in dedicated NMR laboratories. The size of the superconducting magnets, their sensitivity to harsh environments, and the cost of maintenance and operation keep this technology away from fume hoods and production sites, where simpler devices that provide access to medium-size molecules would be needed.

Robust NMR magnets can be made from permanent magnets like those used for NMR spectroscopy in the 1960s and 1970s. But to achieve high resolution for standard sample volumes, the permanent magnets then were as big as superconducting magnets today and weighed several hundred kilograms. Considering that the magnetic field strength remains constant when the volume of the magnet is scaled down to gain portability and that fields of up to 2 T are generated by permanent magnets, small magnets would offer a sensitivity only a factor of three smaller than that achieved in a standard (7 T) superconducting magnet[1] (see the dotted-dashed lines in Figure 1). This limitation is an affordable price to be paid for a small and portable system. However, a second factor seriously compromises the signal-to-noise ratio in the miniaturization process: the reduction of sample volume.

For each magnet geometry the ratio between the magnet size and the size of the sensitive volume is a constant. When the size of the magnet is reduced, a smaller volume of high-field homogeneity is generated. For example, if the old-fashioned Varian T-60 magnet, with a volume of about 1 m^3, is reduced to palm-size dimensions, a sensitivity loss of about three orders of magnitude is expected (circle in Figure 1). Although this approach is valid in cases where the amount of sample is limited (capillary NMR), this sensitivity loss is simply unacceptable for most applications.

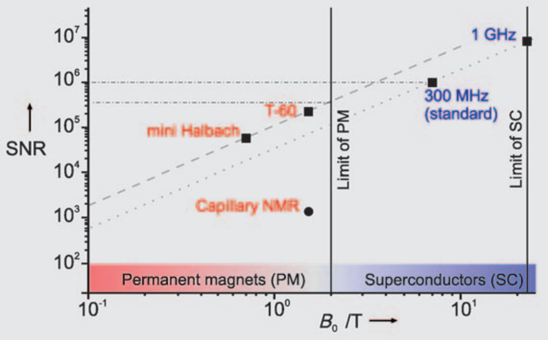

Figure 1. Signal-to-noise ratio (SNR) for permanent and superconducting magnets as a function of the field strength B_0. Squares show the SNR for water in a 5 mm NMR tube. Dashed and dotted lines correspond to solenoidal and birdcage rf coils used with permanent and superconducting magnets, respectively.[1] The circle indicates the SNR value for a reduced sample volume in a capillary with a diameter of 0.3 mm.[2]

We report herein on the construction of a small permanent magnet with an extraordinarily homogeneous magnetic field B_0 suitable for measuring ^{1}H NMR spectra of solutions in standard 5 mm NMR sample tubes (Figure 2). Weighing only 500 grams, the magnet can be transported along with the spectrometer, and NMR measurements can be performed on demand with this robust device at minimal maintenance cost.

To efficiently reduce the sensor volume by three orders of magnitude over that of typical C-magnet designs, individual magnet blocks were compactly arranged in a cylindrical array based on the design by Halbach.[3] This array provides a generous volume for sample positioning (large bore/magnet size ratio), and generates a magnetic field perpendicular to its cylinder axis (Figure 2), which allows the use of sensitive solenoidal radio-frequency (rf) coils to detect the NMR signals. In theory, the magnetic field generated by an infinitely long magnet built from perfect magnet blocks would be highly homogeneous along the length of the sample tube with almost zero stray field. However, in practice, the finite length of the magnet and the statistical imperfections of the sintered magnet blocks deteriorate the predicted homogeneity by several orders of magnitude.[4]

The new design presented herein combines three Halbach rings with different geometric proportions optimized to account for the field distortions along the cylinder axis due to the finite magnet length. To tackle the important source of inhomogeneity introduced by the variability of the pieces, each ring is composed of fixed trapezoidal elements with parallel gaps between them that guide the movement of rectangular magnet blocks (Figure 2). These pieces can be moved radially in and out to mechanically shim the magnetic field with highly efficiency and accuracy.[5] By displacing the rectangular blocks in each ring with defined angular modulations and amplitudes, it is possible to independently

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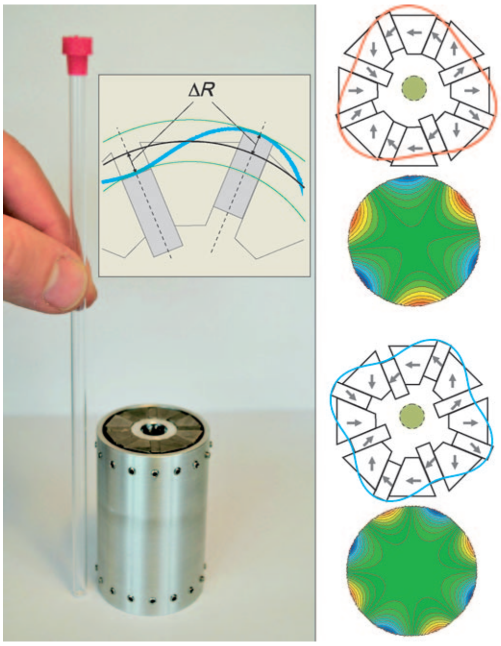

Figure 2. Photograph of the Halbach magnet composed of rectangular and trapezoidal pieces of SmCo which generate a field of 0.7 T. It is 80 mm long and has inner and outer diameters of 15 and 35 mm, respectively. By displacing the rectangular magnets following the modulations shown in the sketches on the right, corrections of third (red) and fourth (blue) order can be generated as illustrated by the two-dimensional field maps underneath. The inset shows the amplitude of the movements Δ*R* of the rectangular magnets, which are the control variable for the mechanical shimming.

generate the set of spherically harmonic corrections to the magnetic field up to an order of *N*/2, where *N* is the number of rectangular blocks in the ring. As an example, Figure 2 shows the required modulation for the displacements of the rectangular magnets to generate tesseral corrections of orders three (red) and four (blue) together with the corresponding two-dimensional field maps. The shim procedure requires measuring the magnetic field by magnetic resonance imaging (MRI) and projecting it along the spherically harmonic basis set.[6] By adding the displacements required to correct each term, the final positions of the rectangular magnets are obtained.

This modification of the Halbach array was numerically optimized to provide sub-ppm resolution with the smallest cylindrical magnet suitable for experiments using standard 5 mm sample tubes. The movable magnet blocks can be displaced by up to 2 mm with a precision of about 1 μm; this results in the range of shim corrections ΔB_n illustrated in Figure 3 for spherical harmonic functions of different orders measured at the edge of the sample ($r = 2$ mm). It is interesting to notice the linearity between ΔB_n and the amplitude ΔR of the movement of the rectangular magnets as defined in Figure 2. This behavior is analogous to the dependence of the field correction introduced by resistive coils with varying current strength. To compare the two shimming approaches, the upper abscissa in Figure 3 shows the current values needed to generate identical ΔB_n values with resistive shim coils. Making use of the full displacement range, the shim magnets correct inhomogeneities of the order of 20000 ppm, a limit that is unreachable for electrical shims because of the excessive current strengths required (blue region). On the other hand, the accuracy of the mechanical shimming procedure in the ppm range is limited by the mechanical precision in moving the rectangular pieces. The deviation in the magnetic field corrections arising from the mechanical imprecision becomes smaller for corrections of increasing order *n* (circles in Figure 3). So, while the first and second shim orders would require the fine-tuning provided by electrical shims, mechanical shimming provides high performance in the sub-ppm range for higher orders.

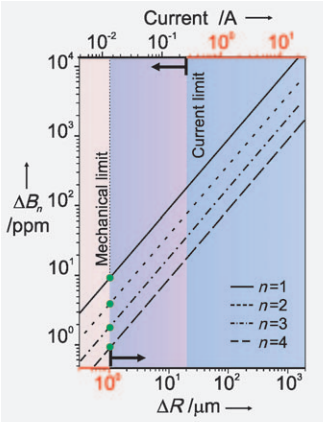

Figure 3. Efficiency and precision of mechanical and resistive-coil shimming approaches. Strength of the magnetic field correction of order *n* as a function of the control variable Δ*R* for the mechanical shim. The upper abscissa shows the currents needed to generate identical corrections using resistive coils. Once the homogeneity limit imposed by the mechanical precision is reached, further improvements can be achieved with electrical shims and currents of few milliamperes (pink region).

The homogeneity achieved with this magnet is evident in the spectra of water and toluene acquired in a 5 mm NMR tube (Figure 4). The line width at half height of 4.5 Hz (0.15 ppm) was achieved with the bare magnet, where only gradient coils were used for finer field adjustment of the first-

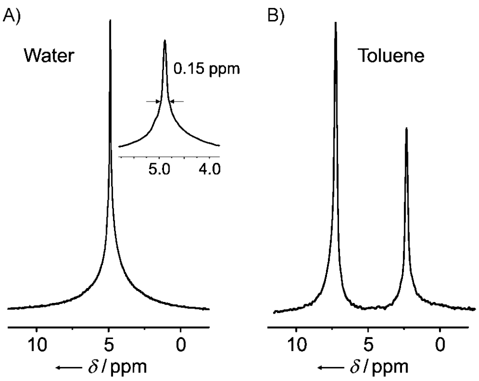

Figure 4. A) Spectrum of water in a conventional 5 mm NMR tube. The spectrum is the Fourier transform of the free induction decay of 16 scans acquired during an acquisition time of 536 ms with a recycle delay of 10 s. B) Spectrum of toluene obtained after Fourier transformation of the free induction decay of 64 scans.

order terms. These results demonstrate that homogeneous miniature magnets suitable for high-resolution NMR spectroscopy of regular-size NMR samples can be built from several imperfect permanent magnet blocks. As the magnet system requires extremely low power, it could be operated in the future with batteries and single-chip electronics,[7] so that high-resolution NMR spectrometers will become portable tools to analyze samples anywhere.

Further improvements in the strength, size, homogeneity, and temperature stability of the magnet are a matter of technological refinement. A higher field can be achieved by increasing the outer diameter of the magnet array. For magnets built from SmCo, 1.5 T (corresponding to a proton frequency of 60 MHz) can be obtained with an outer diameter of 7.5 cm. This material has better thermal stability than NdFeB, but remaining field drifts arising from fluctuations of the magnet temperature must still be eliminated, for example, by combining standard temperature control schemes with a field-frequency lock. NdFeB magnets can yield field strengths as high as 2 T, which would set the upper field limit for this array. Better homogeneity can be obtained by additional use of electrical shim coils driven with a few tens of milliamperes of current, which further reduce the remnant field inhomogeneities beyond the limit imposed by the accuracy of mechanical movements (see pink region in Figure 3). Once this homogeneity limit is reached, powerful pulse sequences can be implemented to achieve further compensation for spatial dependence and temporal instabilities of the magnetic detection field.[8] Finally, different technologies for sensitivity enhancement are being developed that may benefit compact miniature NMR spectroscopy to be useful also for analysis of larger molecules, smaller concentrations, and less sensitive nuclei.[9]

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