Journal of Magnetic Resonance 258 (2015) 1–5

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Communication

Susceptibility cancellation of a microcoil wound with a paramagnetic-liquid-filled copper capillary

Kazuyuki Takeda *, Tomoya Takasaki, K. Takegoshi

Division of Chemistry, Graduate School of Science, Kyoto University, 606-8502 Kyoto, Japan

ARTICLE INFO

Article history:
Received 22 April 2015
Revised 9 June 2015
Available online 22 June 2015

Keywords:
Microcoil
Bulk magnetic susceptibility
Copper capillary
Paramagnetic liquid
Susceptibility cancellation

ABSTRACT

Even though microcoils improve the sensitivity of NMR measurement of tiny samples, magnetic-field inhomogeneity due to the bulk susceptibility effect of the coil material can cause serious resonance-line broadening. Here, we propose to fabricate the microcoil using a thin, hollow copper capillary instead of a wire and fill paramagnetic liquid inside the capillary, so as to cancel the diamagnetic contribution of the copper. Susceptibility cancellation is demonstrated using aqueous solution of $NiSO_4$. In addition, the paramagnetic liquid serves as coolant when it is circulated through the copper capillary, effectively transferring the heat generated by radiofrequency pulses.

For NMR measurements of mass-limited samples, a microcoil is advantageous in terms of the sensitivity [1,2], while the price to pay is the reduced spectral resolution due to magnetic-field inhomogeneity caused by the bulk susceptibility effect (BMS) of the coil wire [2]. In general, a body with non-zero magnetic susceptibility is magnetized in the presence of an external magnetic field. As a consequence, an additional perturbative field arises in the vicinity of the body. Since the strength of the induced field decreases rapidly with the distance, the BMS effect is relatively small for NMR measurements using sample coils with the conventional size. However, in the case of the microcoils, the sample is inevitably close to the coil wire. Thus, the BMS effect can cause significant line broadening.

Copper, which is used for the coil material in many cases, is diamagnetic, so that a magnetization antiparallel to the external field develops. The profile of the induced magnetic field is determined by the geometry of the coil. In the case of a solenoid coil, the resultant field distribution contains high-order terms that are difficult to remove by the standard shimming technique.

So far, several schemes to suppress the BMS-induced field inhomogeneity have been proposed [3]. They include susceptibility matching [2,4,5], zero-susceptibility wire [6–8], and magic-angle coil spinning (MACS) [9–11]. It is also worth noting that the effect of susceptibility broadening is small in stripline probes [12,13]. Here, we report an alternative approach. Our idea is to make a microcoil with a thin capillary made of copper and to fill paramagnetic liquid solution inside the capillary. We aim at cancelling the diamagnetic contribution of the copper.

Our scheme, which is similar to that of zero-susceptibility wire, has a noteworthy feature that the net susceptibility can be modified simply by changing the concentration of the paramagnetic solute. This contrasts with the case of the zero-susceptibility wire, where such fine adjustment is formidable. Indeed, when Hoult and Ginsberg used a commercial zero-susceptibility wire in their studies on nuclear spin noise, they had to do an elaborate job of electroplating an additional copper layer, as they found that the diameter of their copper-clad aluminum-core wire differed significantly from the nominal value [14]. In addition, the paramagnetic liquid can flow through the capillary, serving as effective coolant, as demonstrated below.

Thin copper capillaries are used for the electrodes of discharge machining devices and are commercially available. In this work, we used one with an outer diameter of 0.2 mm and an inner diameter of 0.1 mm, which was purchased from Nippon Tokushukan MFG. CO., Ltd. Since the copper capillary was fragile, we wound it gently into microcoils so as not to clog the passage. An example of copper-capillary-wound microcoils is shown in Fig. 1(a). Its inner diameter is 0.4 mm, and the number of turns is 8. Using a chip ceramic capacitor for balancing and a pair of surface mount trimmer capacitors (TZC3, Murata Electronics) for impedance matching, we fabricated a tank circuit resonating at ca. 300 MHz on a printed circuit board (Fig. 1(b)). The Q factor of the circuit was measured to be 23. Each end of the coil penetrates the board through a conducting via, at which the electrical connection is established by soldering. To supply liquid, poly ether ether ketone

* Corresponding author.
E-mail address: takezo@kuchem.kyoto-u.ac.jp (K. Takeda).

http://dx.doi.org/10.1016/j.jmr.2015.06.003
1090-7807/

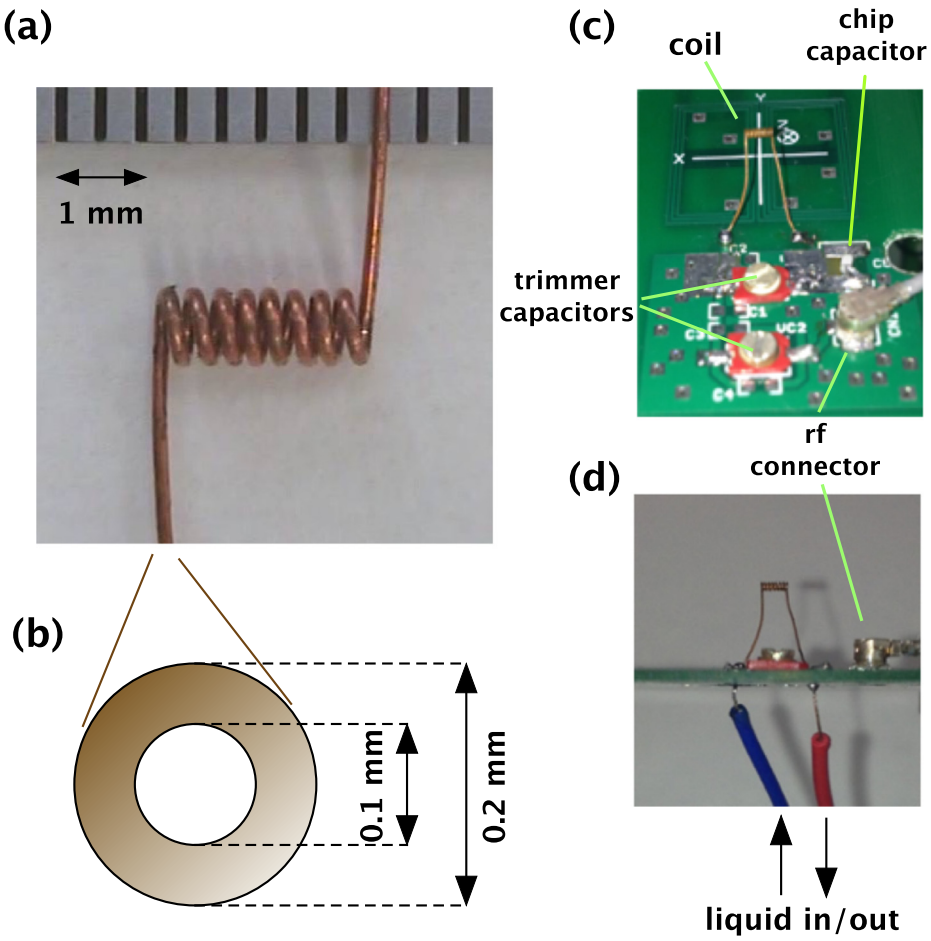

Fig. 1. (a) A photo of a microcoil wound with a copper capillary with an inner diameter of 0.1 mm and an outer diameter of 0.2 mm. (b) Schematic drawing of the cross section of the capillary. (c) A probehead composed of the microcoil, a chip capacitor, and trimmer capacitors. (d) A side view of the probe. Tubes are connected to both end of the copper capillary to supply liquid.

(PEEK) tubes were connected at both ends of the copper capillary (Fig. 1(c)).

For paramagnetic liquid, we used aqueous solution of $NiSO_4$. For molar concentration α, the susceptibility at room temperature is given by $50.3\alpha \times 10^{-6}$ in SI unit, while the susceptibility of our microcoil was measured to be -10.6×10^{-6} (*vide infra*). Since the volume fraction of the hollow region of the capillary is 25%, we naively estimated the concentration α that annuls the net susceptibility to be 0.63 M.

The standard electrode potentials for nickel and copper are −0.23 V and +0.35 V, respectively. Since the ionization tendency increases with the negative potential, $Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$, rather than $Ni^{2+} + Cu \rightarrow Ni + Cu^{2+}$, is favoured thermodynamically. Thus, dissolution of copper into the $NiSO_4$ solution is thermodynamically unfavorable.

^{1}H NMR measurements were performed using a 7 T superconducting magnet at room temperature. The carrier frequency was 299.52 MHz. First, we carried out experiments with the microcoil without filling liquid inside the capillary. Fig. 2(a) shows a ^{1}H spectrum of 0.1 M aqueous solution of $CuSO_4$ in a quartz tube with an inner/outer diameter of 0.2/0.4 mm. We found considerable broadening and distortion in the spectrum acquired with the microcoil, which were caused by the BMS effect of the microcoil. The full width at half maximum was 93 Hz. For comparison, we also acquired a ^{1}H NMR spectrum of the same sample using a microcoil of the same geometry but wound with a solid copper wire with a diameter of 0.2 mm (Fig. 2(b)). We found that the sensitivity was comparable for both coils, while the broadening and distortion of the resonance line were less appreciable for the capillary-wound microcoil. In addition, we measured ^{1}H NMR of the same sample using a larger coil with a diameter of 5 mm (Fig. 2(c)). Here, the origin of the line width (38 Hz) was ascribed to the field inhomogeneity of our 7 T magnet used in the present study.

Next, we performed experiments by supplying aqueous solution of $NiSO_4$ inside the copper capillary. No background ^{1}H signal due to the paramagnetic liquid was observed. As demonstrated in Fig. 3(a), the line width of the ^{1}H spectrum decreased with the concentration of $NiSO_4$, reached the minimum (52 Hz) at 0.54 M. With increasing the $NiSO_4$ concentration further, the spectral resolution degraded, because the paramagnetic contribution became too strong. As shown in Fig. 3(b), with the optimal concentration, the peak height was enhanced by 58% compared to that in the case of pure water (i.e., no $NiSO_4$ dissolved). In addition, with increasing the overall paramagnetic contribution, the resonance line shifted to higher frequencies (Fig. 3(c)).

The optimal $NiSO_4$ concentration of 0.54 M was ca. 14% smaller than the estimated value of 0.63 M. In order to discuss the difference, we performed numerical analysis as follows. The longitudinal component $b_z(\mathbf{r};\mathbf{r}')$ of the magnetic field produced at point $\mathbf{r} = (x, y, z)$ by an infinitesimal magnetization $\mathbf{m}(\mathbf{r}')d\mathbf{r}'$ at point $\mathbf{r}' = (x', y', z')$ is given by