LLNL-PROC-409793

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January 12, 2009

Magnetic Resonance in Porous Media
Cambridge, MA, United States
July 13, 2008 through July 17, 2008

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Low Cost CE-NMR with Microcoils for Chemical Detection

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(received 27 July 2008, accepted 28 July 2008)

Abstract

Understanding speciation in solids and solutions is important for environmental and toxicological purposes. Capillary electrophoresis (CE) is a simple rapid separation technique that can be used to identify species in solution. CE is particularly is well suited for rapid separations of metal containing samples. Direct on-capillary measurement of metal compound speciation can be obtained with nuclear magnetic resonance (NMR). The development of a low-cost microcoil CE-NMR system for in situ characterization of samples of interest is discussed. High precision laser lithography is used to produce copper sputtered microcoils that have comparable resistivity and quality factors to that of hand wound microcoils. A portable NMR system coupled with a CE system has the potential to identify chemical species in aqueous solutions. In addition, transient isotachophoresis can separate and pre-concentrate samples of interest to obtain separate chemical peaks for speciation by online NMR analysis. We are developing separation assays to determine the speciation of chemical complexes in solutions with minimal perturbation to the original sample equilibrium. On-line NMR measurements will be made downstream of the UV detector. **Copyrights** remain with the Authors.

Keywords - portable NMR, lithographic microcoils, capillary electrophoresis, CE, metal speciation, isotachophoresis

1. LLNL Laser Lithography Process and RF Microcoil Probe Development

Laser lithographic techniques are used to design and construct radio frequency (RF) copper microcoils patterned onto capillaries for portable NMR probes [1, 2]. Microcoils are developed onto the capillaries by standard lithographic techniques (see Figure 1). The capillaries are first coated with copper and photoresist layers. Then, the Laser Lithography (L-Lathe) system etches the coil pattern by ablating the photoresist down to the lower copper layer in specifically designed patterns. The copper is then electroplated into the laser etched pattern. And finally the remaining photoresist mask and thin copper layer directly below this mask are lithographically removed leaving a precisely designed, highly reproducible copper microcoil. The L-Lathe process can produce solenoidal coils of varying OD, windings, thickness, pitch, and more complicated 3D shaped microcoil.

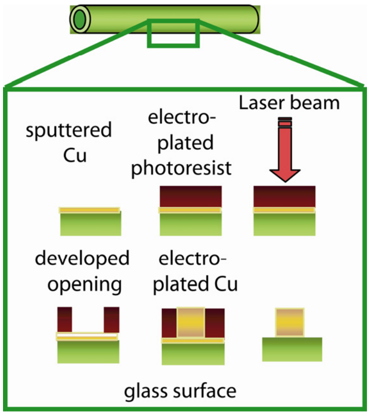

Fig 1. L-Lathe process for creating solenoidal lithographic RF copper microcoils on a capillary surface.

1.1. Microcoil Electronic Characterization

Electronic characterization of the lithographically patterned microcoils demonstrates the versatility of the production method. The resistivity of the lithographic coils (1.85 mΩ·cm) is comparable to that of hand wound copper wire coils (1.72 mΩ·cm) of identical size [1]. Measurements show that increasing the electroplated microcoil thickness will decrease resistance and increase the signal to noise ratio [3].

Recent data [3] also shows lithographic microcoils of certain dimensions can exhibit lower resistivity and better quality factors than wire coils wound with a motor controlled system. Lithographic microcoils are compared in several configurations, including varying thickness, pitch, diameter, and winding number as well as compared to similar motor-wound wire coils. In addition, 2-D Ansofts Maxwell simulations of current distributions in RF coils are run on both square and round coil cross-sections; results show the solenoidal inner surface, carries the highest current loads for small OD microcoils.

2. NMR RF Microcoil Probe Design Provides Durability and Flexibility

The portable NMR probe is designed to be easily interchangeable (see Figure 2), to facilitate probe exchange for the testing of various microcoils without the need to replace the tuning circuitry each time. The RF microcoil is etched onto a capillary that removes with the interchangeable probe. The capillary and microcoil are jacketed in copper tubing to enhance durability and to extend the RF microcoil into the center of the magnetic field. Lithographic shimming coils may be added to a ceramic collar surrounding the RF coil to improve magnetic field homogeneity (Figure 2). The probe and circuitry are mounted on a triple axis micrometer stage to allow for centering of the RF microcoil in the magnetic field.

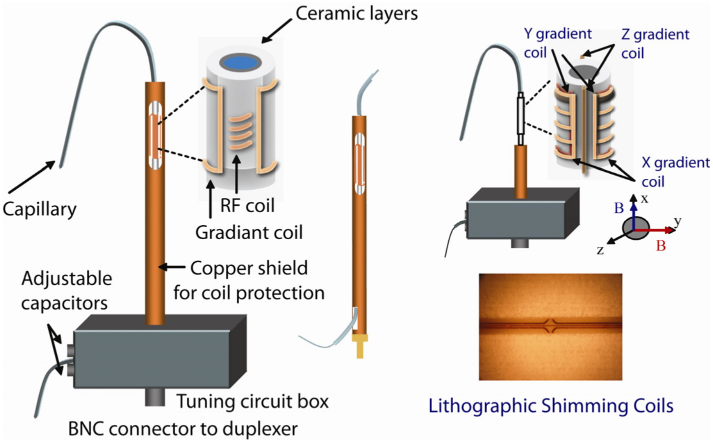

Fig 2. Portable NMR probe design showing exchangeable probe with lithographic RF microcoils and lithographic microcoil shimming design shown on outer ceramic collar.

3. Portable magnet evaluation

Several low field portable magnets have been evaluated including 1T and 2T Magnetic Solutions Halbach magnets, 1T and 1.7T Aster Enterprises box magnets, and a 0.4T Tecmag multi-ring Halbach magnet. The Magnetic Solutions Halbach magnets show best overall uniformity achieving good fits with quadratic terms (Figure 3a). The Aster magnets show a less uniform overall field (Figure 3a) but exhibit excellent shielding important for a portable system and uniform magnetic fields in the magnets' center bore. A comparison of ppm resolution for ^{19}F NMR of flourinert in the frequency domain for high field and three low field portable Aster box magnets is shown in Figure 3b. The 1.7T Aster box magnet exhibits 1-2 ppm resolution, though signal-to-noise improvements are still desired. We believe the discrepancy between signal-to-noise comparisons of the 1.7T magnet and the 1T magnet may be due to the probe copper housing touching the inner bore of the 1.7T magnet as the larger magnet radius requires the NMR probe to be inserted further into the 1.7T magnet to be centered in the field and deviations in the copper diameter need to be addressed to eliminate excess electronic noise.

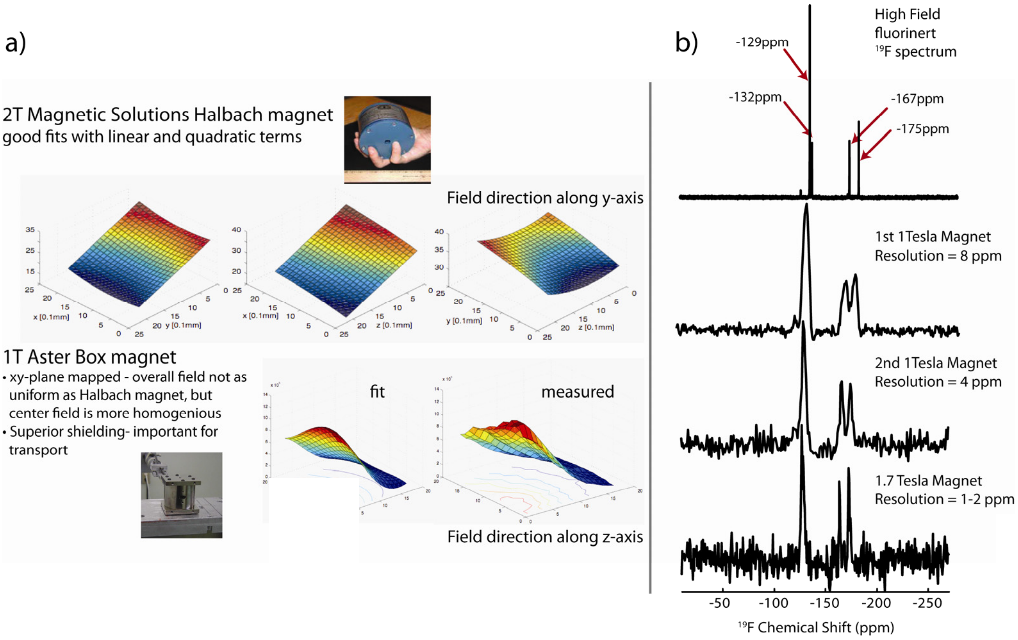

Fig 3. a) Magnetic field maps of 2T Magnetic Solutions Halbach magnet and 1T Aster Enterprises Box magnet. b) Comparison of ppm resolution using ^{19}F NMR of flourinert in the frequency domain for high field and three low field portable Aster box magnets, two 1T and one 1.7T magnet. Data obtained with 410µm OD, 320µm ID 410µm length microcoil, and 28 scans with a 0.5 second delay time.

The portable NMR system is greatly affected by room temperature stability. Figure 4 shows temperature variations observed overnight in two environments: a) room with widely varying temperature shifts (ΔT > 2.8˚C observed in a 10 minute interval) and b) temperature controlled room with temperature shifts less than 0.28˚C during a 24 hour interval. Data was taken on the same sample repeatedly overnight with an hour delay between each 28 scan data set. Large temperature variations produce large peak shifts, Figure 4a) shows line shifts greater than 100 ppm. However, even small temperature variations shown in Figure 4b) exhibit line shifts of 9 ppm. Dilute samples requiring integration times longer than a few seconds will suffer line broadening in environments with changing temperatures. Further work is needed to negate the observed temperature drifting as the portable NMR system must function in field environments with varying conditions. Several solutions are being investigated, including adding a deuterium lock channel on top of the current shim coil geometry, adding a PID temperature controller and magnet insulation, and using magnets designed with temperature compensating materials such as Samarium cobalt (SmCo). The current box magnets have a Hiperco Alloy 50A (nickel-cobalt-vanadium) magnet material with thermal coefficient of 0.035%/°C where SmCo has a thermal coffecient of -0.001%/°C.

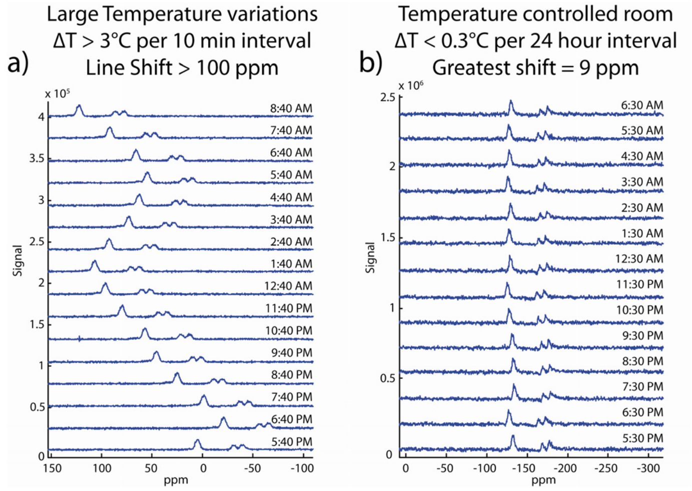

Fig 4. ^{19}F NMR of flourinert in the frequency domain taken on Aster 1.7T magnet with 28 scans and delay time = 0.5s. Data was taken overnight with a 1 hour delay between scan sets in: a) room with temperature variations observed greater than 2.8˚C in a 10 minute interval, b) room with temperature stability within 0.28˚C over a 24 hour interval. Note that magnet temperature does not vary as greatly as room temperature.

Capillary electrophoresis (CE) is being investigated to provide sample pre-concentration and separation. Transient isotachophoresis [4], a CE stacking technique, can separate and pre-concentrate individual chemicals based on molecular size and charge. NMR can then provide additional speciation information by centering one of these chemical plugs in the RF microcoil. The CE will provide a specific chemical plug of interest, pre-concentrated to the online portable NMR where speciation of the chemical of interest can occur.

4. Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

1. Malba, V., et al., *Biomedical Microdevices* **5** (1), 21-27 (2003).
2. Demas, V., et al., *Journal of Magnetic Resonance* **189** (1), 121-129 (2007).
3. Demas, V., et al., Manuscript in progress.
4. Church, M.N., et al., *Analytical Chemistry* **70** (13), 2475-2480 (1998).