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# Portable, low-cost NMR with laser-lathe lithography produced microcoils

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**Abstract**

Nuclear Magnetic Resonance (NMR) is unsurpassed in its ability to non-destructively probe chemical identity. Portable, low-cost NMR sensors would enable on-site identification of potentially hazardous substances, as well as the study of samples in a variety of industrial applications. Recent developments in RF microcoil construction (i.e. coils much smaller than the standard 5 mm NMR RF coils), have dramatically increased NMR sensitivity and decreased the limits-of-detection (LOD). We are using advances in laser pantographic microfabrication techniques, unique to LLNL, to produce RF microcoils for field deployable, high sensitivity NMR-based detectors. This same fabrication technique can be used to produce imaging coils for MRI as well as for standard hardware shimming or "ex-situ" shimming of field inhomogeneities typically associated with inexpensive magnets.

This paper describes a portable NMR system based on the use of a 2 kg hand-held permanent magnet, laser-fabricated microcoils, and a compact spectrometer. The main limitations for such a system are the low resolution and sensitivity associated with the low field values and quality of small permanent magnets, as well as the lack of large amounts of sample of interest in most cases. The focus of the paper is on the setting up of this system, initial results, sensitivity measurements, discussion of the limitations and future plans.

The results, even though preliminary, are promising and provide the foundation for developing a portable, inexpensive NMR system for chemical analysis. Such a system will be ideal for chemical identification of trace substances on site.
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## 1. Introduction

The need for portable chemical analysis of suspect analytes in the field, including signatures from production of chemical and biological weapon agents, drugs, explosives, toxins, and poisons is well established. Demand for portable analysis equipment is growing in the defense and intelligence communities and, as a result, a number of field deployable analytical methods are being developed, including mass spectrometric- and infrared-based systems. Still, unambiguous identification of suspect reagents can be difficult because of the dilute concentrations of suspect analytes as well as the typically large background signals from complex mixtures. The unambiguous assignment of molecular signatures to scheduled compounds can be compromised in mass spectrometry by derivitization steps or unexpected chemistry in the high temperatures present in gas chromatographic columns. Nuclear Magnetic Resonance (NMR), however, offers a non-destructive, reagentless analytical method for the identification of suspect analytes. NMR is one of the more important techniques for quantitative analysis [1–3], in no small part because it provides the inherently quantitative spectrum with unique structural information encoded in the chemical shifts and coupling constants

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without the need for precise matching to signature libraries.

Unfortunately, commercial systems are not well suited for portable NMR platforms due to the inherent lack of sensitivity of standard NMR receiver coils and the bulky size of the associated superconducting magnet. During recent years several groups are developing. Portable NMR systems offer several advantages over conventional NMR, such as scanning in the field, access to immovable, arbitrary-sized objects, lower cost, and increased robustness. Existing unilateral sensors are now being used routinely to perform NMR imaging and relaxation measurements. Despite the strongly inhomogeneous fields, devices such as the NMR MOUSE [4–9], and other unilateral or inside-out sensors [10–16] are being used for applications ranging from materials (e.g. mechanical properties of polymers, fat content of dairy products) and tissue evaluation [17–25] to flow measurements [26,27], art preservation [28,29] and oil well logging [30,31]. However, the spatial inhomogeneity of the static magnetic field has precluded the use of such devices for high-resolution spectroscopy.

During the past few years ex-situ methodologies have been developed to obtain high-resolution NMR spectra in the presence of field inhomogeneities, typical of MOUSE-type instruments [32,33], ex-situ shimming [34] and hardware shimming [35] have been used to acquire high-resolution spectra in single-sided systems. The open-sided field geometry, as well as the inherently low static field of such systems, result in a decreased sensitivity relative to laboratory NMR systems.

Microcoils are now used to increase the sensitivity of NMR spectra for mass limited samples [36–42] because the reduced RF coil diameter leads to an increase in the sensitivity of the coil itself [36,37,41,43]. Thus, for mass limited samples, one can obtain a significant increase in signal-to-noise (SNR). Olson et al. [37] have even reported limits of detection to the order of pico-moles. Others use planar microcoils that are made in two-dimensions for NMR experiments, [64] but these systems still lack sensitivity because flat coils are inherently less sensitive than RF coils surrounding the sample. Most solenoidal microcoils are hand-wound with insulated copper wire around a capillary [37,43–47].

Numerous groups have demonstrated effective results with hand-wound microcoils, as shown in some of the cited references in the present paper. However, the goal of our research is to go beyond the current state-of-the art (i.e. wire-wound microcoils) and advance the limits of NMR technologies. Even though hand-wound microcoils have reproducible results, the geometry precision and design flexibility of such coils is limited by human factors. Lithography, the basis of the integrated circuits manufacturing industry, has demonstrated unparallel precision in the construction of electronic devices. We expect these techniques, when developed for three-dimensional geometries, to be far more precise than manually produced microcoils. Rogers et al. [39,40] were the first to employ micro-fabrication techniques (based on a wet-resist transfer method) to manufacture RF coils with variable design parameters. This technique uses photolithographic fabrication of an elastomeric stamp with a series of evenly spaced raised lines. This stamp is then coated with resist or ink, which is transferred to a titanium–silver coated capillary tube by rolling it across a wet line at a specific angle. This process yields RF microcoils that show an increase in SNR in a standard NMR experiment.

We have reported previously on the fabrication of complex design RF microcoils by a 3-dimensional laser direct-write lithographic technique [48]. This technique is used on a variety of micro-devices, including micro-catheters and electrical contacts to diamond anvil cells [49]. We have used this strategy to produce microcoils on the order of 100 μm in diameter. While the properties of our coils are very similar to those described by Sillerud et al. via the focused ion beam lathe for microcoil fabrication [50], we have the ability to control to a larger extent the fabrication process and therefore are able to achieve more desirable characteristics (e.g. thicker deposition corresponds to lower direct current resistance), as well as complex shapes. Our fabrication process and electrical characterization of these microcoils are discussed elsewhere [48,51].

As described in Ref. [52], a portable NMR system based on microcoil technology has numerous advantages. First, the sensitivity of the system increases as the sample volume decreases (a conventional system using a 5 mm diameter RF coil can detect $10^{17}$ spins while 100 μm coils can detect $10^{12}$ spins [44]). Second, the power needed to efficiently excite nuclei decreases by orders of magnitude, reducing the need for large RF amplifiers [53]. Third, the need for the large regions of field homogeneity produced by superconducting magnets is eliminated due to the drastic decrease in sample volume, thus permitting the use of small permanent magnets (NdFeB and SmCo magnets can produce fields of 2 T in a 1 kg package). At 2 T, the proton Larmor Frequency is 85 MHz, which is quite acceptable for the identification of low molecular weight compounds, considering that 90 MHz was the frequency of the standard laboratory-size NMR in the 1980s.

The small portable, permanent magnets, such as Halbach- and barrel-based, U-shaped, and dipoles, are unfortunately characterized by complex magnetic field profiles requiring field compensation via pole shaping, magnetic shims or shim coils. Their small size further requires a large amount of RF circuitry to be fit in a restricted space. The design and construction of such coils is ill-suited to typical construction methods, but becomes feasible with LLNLs unique microfabrication methods [48]. In a similar fashion, this lithography method affords the integrated design and manufacturing of combined receiver, shim, and gradient coils, as well as flow and multiplex capabilities in a compact package. These advantages of LLNL lithographic fabrication allow the production of microcoils for portable, high resolution, high sensitivity NMR.