# Measurement of Magnetic Particle Concentrations in Wildfire Ash via Compact NMR

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Abstract—Wildfire ash plumes deposit magnetic particles (nanoscale and larger) into rivers and streams. Post-fire runoff contains increased levels of suspended particles and contaminants; including traces of metals, nutrients, and total suspended solids that affect the water quality and aquatic species. This work reports on a compact and portable Nuclear Magnetic Resonance (NMR) system capable of measuring the magnetic particle content in wildfire ash. The system is comprised of a custom NMR device with a specially designed permanent magnet that shapes the magnetic field to provide the basis of a compact and robust NMR-based sensing system for the future in-field measurements of ash in aqueous solutions. The system is set up to measure transverse relaxation processes and can acquire sufficient data in as little as two minutes. Experimental results confirmed the linear relationship between magnetic content in water and transverse relaxation rates, and can therefore be used as a method for estimating magnetic content in wildfire ash.

*Index Terms*—NMR, magnetic particle, RF, permanent magnet, ash, wildfire

## I. INTRODUCTION

Nuclear Magnetic Resonance (NMR) devices allow for the characterization and analysis of systems in a quick, nondestructive fashion and often require little to no sample preparation. Although NMR spectroscopy that utilizes Fourier analysis tends to be the most used NMR method due to the ability for high-resolution molecular structure characterization, the sensitivity required is difficult to achieve in a practical way for compact systems. NMR relaxometry, however, focuses on the relaxation processes in a sample as a function of time and requires much lower system sensitivity in order to acquire useful results [1]. This combined with constant advancements in the size and quality of electronics has allowed for the ability to develop simple, lab-built time-domain NMR (TD-NMR) systems that can be customized for specific applications [2].

While proton NMR is typically used to identify molecular structures directly attached to hydrogen atoms, it can also provide information about the environment surrounding the hydrogen nuclei [3]. One such case is water containing magnetic particles (MPs), and it has been shown in previous work that longitudinal and transverse  $(R_1 \text{ and } R_2)$  water relaxivity shifts are directly correlated to MP concentrations [4], [5]. NMR techniques involving MPs are largely used for biomedical imaging and diagnostics [6], [7], but their usefulness can also be extended to environmental applications. One possibility is the characterization of wildfire ash. Ash can contain and deposit varying levels of MPs into the soil and surrounding bodies of water, and measurements of these particles can help assess wildfire severity and the content of main soil nutrients [8], [9]. Furthermore, a simple and rapid method for the in situ measuring of magnetic content in ash can be very useful.

Here we present a compact TD-NMR design capable of estimating MP concentrations for wildfire ash samples dissolved in water. The system can perform quick, non-invasive tests that require small sample sizes. The contributions of this paper are twofold: (1) showing that magnetic content in ash can be measured using a benchtop TD-NMR device and; (2) demonstrating the capabilities of a TD-NMR system with a simple, low-cost permanent magnet array suitable for 5 mm sample sizes.

## II. SYSTEM DESIGN

Fig. 1(a) shows the compact TD-NMR system, and the full schematic can be seen in Fig. 1(b). A laptop with LabVIEW programming is used to calibrate to the correct frequency, generate the waveforms needed to run tests, and export data. The laptop connects to a NI PXI chassis and the chassis

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Fig. 1. The Benchtop compact TD-NMR system, showing: (a) system setup with key items annotated, and; (b) schematic for the control system and RF electronics.

is connected to the custom electronics with 50  $\Omega$  cables. All signal routing and amplification components are mounted on PCBs except for the high-power RF amplifier and lownoise RF amplifier (LNA). The system is designed for testing samples in standard 5 mm NMR tubes.

## A. Signal processing & Amplification Electronics

The schematic for the electronics used in the system is shown in Fig. 1(b). The PCBs were fitted with SMA ports and traces that have been matched to 50  $\Omega$  where needed. The system requires one 24 V power supply that is split between the RF power amplifier and a PCB equipped with linear regulators to step it down to 12 V, 5 V, and 1.8 V for the other components. A sinusoid at the optimal Larmor frequency is driven into a power splitter and sent to the switch and LO port of the mixer. The switch is toggled on and off using a pulse train from the PXI chassis, which is timed according to the Carr-Purcell-Meiboom-Gill pulse sequence [10]. The pulsed RF signal is then amplified to 35 dBm before entering the duplexer and probe, where a Pi filter blocks the large power pulse from damaging the first LNA [11]. The NMR probe consists of a solenoidal coil made of Kapton insulated copper wire and two adjustable capacitors for tuning the probe. After exciting the sample, the response travels through the duplexer, gets amplified by 40 dB at the first LNA stage, and is then mixed down to the range of audio frequencies in order to simplify the next stage of filtering and amplification. The signal is then amplified by another 40 dB and filtered using an analog bandpass of 5-15 kHz before being sent to the digitizer.

#### B. Permanent Magnet Array

In order to generate a sufficiently strong and homogeneous static magnetic field needed for the system, a design that uses ten grade N42 NdFeB permanent magnets was implemented. Two  $1.5 \times 1.5 \times 0.5$  in thick magnets and eight  $1.5 \times 0.25 \times 0.25$  in thick magnets were assembled as shown in Fig. 2. There are 0.5 in thick 1018 carbon steel bars surrounding it to act as a return path for the magnetic flux, and 0.25 in thick 1018 steel caps were placed on the magnet faces to further improve homogeneity inside the gap

[12], [13]. Two-dimensional simulations were performed using Finite Element Method Magnetics to estimate the field before final assembly, which can seen in Fig. 2(c) [14]. 3D printed parts were used to guide the pieces and secure them in the correct locations during assembly. At room temperature, the configuration produces a static field strength of 0.565 T, which corresponds to a Larmor frequency of about 24 MHz. The fully assembled magnet is robust, safe to handle, and weighs approximately 4.4 lbs.

# C. Signal Generation, Control, & Data Acquisition

The signal generation, control, and data acquisition portion of the system consists primarily of a NI PXI chassis that contains a pulse train generator, arbitrary waveform generator, and 16-bit digitizer. LabVIEW was used to create a program that can control the timing of the waveforms, and it has a GUI in the front end for simple control. Temperature affects the field strength of the magnet, and therefore the Larmor frequency, so the program calibrates to the optimal frequency before running a test. The pulse train shapes the sinusoid driven into the switch, with a 6  $\mu$ s pulse time being equivalent to a  $90^{\circ}$  flip of the magnetization vector within the sample. The tau value, which is the delay between the  $90^{\circ}$  and  $180^{\circ}$ pulse, is 1.25 ms and there are 1980 pulses per scan, leading to a scan length of 2.5 s. The relaxation delay between scans is 10 s, so to average 8 scans of a sample it only takes 2 min. The program picks out the peak voltage of each spin echo and plots it as a function of time, which can be modeled by the following:

$$M_{\rm xy}(t) = M_0 \exp(-R_2 t) \tag{1}$$

where the initial magnetization is  $M_0$ , the magnetization at time t is  $M_{xy}(t)$ , and the transverse relaxation rate is  $R_2$ .

# **III. RESULTS & DISCUSSION**

In order to verify that the TD-NMR system could estimate MP concentrations accurately, a synchrotron was used to analyze several ash samples to determine the overall magnetic content in units of mg/g. The wildfire ash samples were then



Fig. 2. The magnet array, showing: (a) fully assembled magnet; (b) orientation of individual magnets and steel pieces, and; (c) two-dimensional finite element simulation.



Fig. 3. Results, showing: (a) T2 relaxation curves for distilled water and three ash samples of varying color, and; (b) linear correlation of relaxation rate R2 and MP concentration measured by synchrotron for various wildfire ash samples suspended in water.

prepared for the TD-NMR device with 20 mg of ash in 20 mL of distilled water and sonicated before being transferred to 5 mm tubes (Norell XR-55). A sample of pure distilled water was tested and recorded in order to establish a basis for the relaxation rate with no MPs present. Fig. 3(a) shows the decay curves for distilled water and a few ash samples with different colors and magnetic content. After testing ten total ash samples, the decay rates were extracted according to (1) via least squares regression and plotted against the MP concentrations determined using synchrotron analysis. This plot can be seen in Fig. 3(b), and it shows the linear relationship

that was expected between the transverse relaxation rate and the MP concentration. The  $R^2$  value indicates that the linear fit is a good approximation for how the magnetic content of water affects the relaxation rate.

### IV. CONCLUSION

This work shows the potential for constructing a simple TD-NMR system that can be used as an environmental sensor. A robust and low-cost permanent magnet design capable of producing a static field sufficient for 5 mm NMR tubes was presented, along with the electronics needed to route and amplify the RF pulses and NMR signal output. The system displays a simple and rapid method for estimating MP content in wildfire ash suspended in water, and a device such as this could be useful for determining how widespread the effects of ash deposits are on surrounding bodies of water and soil. Future work will be dedicated to developing the system so that it can be deployed in fire-impacted areas for in situ monitoring of magnetic content in surface water and soil.

#### REFERENCES

- [1] Blümich, B., 2019. "Low-field and benchtop nmr". *Journal of Magnetic Resonance*, **306**, pp. 27–35.
- [2] Zalesskiy, S. S., Danieli, E., Blümich, B., and Ananikov, V. P., 2014. "Miniaturization of nmr systems: Desktop spectrometers, microcoil spectroscopy, and "nmr on a chip" for chemistry, biochemistry, and industry". *Chemical Reviews*, *114*(11), Jun, pp. 5641–5694.
- [3] Marbella, L. E., and Millstone, J. E., 2015. "Nmr techniques for noble metal nanoparticles". *Chemistry of Materials*, 27(8), pp. 2721–2739.
- [4] Gunn, J., Paranji, R. K., and Zhang, M., 2009. "A simple and highly sensitive method for magnetic nanoparticle quantitation using 1H-NMR spectroscopy". *Biophys J*, 97(9), Nov., pp. 2640–2647.
- [5] Minin, A. S., Uymin, M. A., Yermakov, A. Y., Byzov, I. V., Mysik, A. A., Rayev, M. B., Khramtsov, P. V., Zhakov, S. V., Volegov, A. V., and Zubarev, I. V., 2019. "Application of NMR for quantification of magnetic nanoparticles and development of paper-based assay". *Journal* of *Physics: Conference Series*, 1389(1), nov, p. 012069.
- [6] Shao, H., Yoon, T.-J., Liong, M., Weissleder, R., and Lee, H., 2010. "Magnetic nanoparticles for biomedical NMR-based diagnostics". *Beilstein J Nanotechnol*, *I*, Dec., pp. 142–154.
- [7] Sun, N., Yoon, T.-J., Lee, H., Andress, W., Weissleder, R., and Ham, D., 2011. "Palm nmr and 1-chip nmr". *IEEE Journal of Solid-State Circuits*, 46(1), pp. 342–352.
- [8] Till, J. L., Moskowitz, B., and Poulton, S. W., 2021. "Magnetic properties of plant ashes and their influence on magnetic signatures of fire in soils". *Frontiers in Earth Science*, 8.
- [9] Jordanova, N., Jordanova, D., and Barrón, V., 2019. "Wildfire severity and its environmental effects revealed by soil magnetic properties". *Land Degradation & Development*, 30, 07.
- [10] P. McIntosh, L., 2013. CPMG. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 386–386.
- [11] Louis-Joseph, A., and Lesot, P., 2019. "Designing and building a low-cost portable ft-nmr spectrometer in 2019: A modern challenge". *Comptes Rendus Chimie*, 22(9), pp. 695–711.
- [12] Moresi, G., and Magin, R., 2003. "Miniature permanent magnet for table-top nmr". Concepts in Magnetic Resonance Part B: Magnetic Resonance Engineering, 19B(1), pp. 35–43.
- [13] Blümich, B., Rehorn, C., and Zia, W., 2018. Magnets for Small-Scale and Portable NMR. John Wiley & Sons, Ltd, ch. 1, pp. 1–20.
- [14] Meeker, D., 2010. "Finite element method magnetics". *FEMM*, *4*(32), p. 162.