



# Evaluation of sandstone surface relaxivity using laser-induced breakdown spectroscopy



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## ABSTRACT

Nuclear magnetic resonance (NMR) relaxometry is a common technique used to assess the pore size of fluid-filled porous materials in a wide variety of fields. However, the NMR signal itself only provides a relative distribution of pore size. To calculate an absolute pore size distribution from the NMR data, the material's surface relaxivity needs to be known. Here, a method is presented using laser-induced breakdown spectroscopy (LIBS) to evaluate surface relaxivity in sandstones. NMR transverse and longitudinal relaxation was measured on a set of sandstone samples and the surface relaxivity was calculated from the pore size distribution determined with MICP measurements. Using multivariate analysis, it was determined that the LIBS data can predict with good accuracy the longitudinal ( $R^2 \sim 0.84$ ) and transverse ( $R^2 \sim 0.79$ ) surface relaxivity. Analysis of the regression coefficients shows significant influence from several elements. Some of these are elements previously established to have an effect on surface relaxivity, such as iron and manganese, while others are not commonly associated with surface relaxivity, such as cobalt and titanium. Furthermore, LIBS provides advantages compared to current methods to calibrate surface relaxivity in terms of speed, portability, and sample size requirements. While this paper focuses on geological samples, the method could potentially be expanded to other types of porous materials.

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## 1. Introduction

NMR has been used extensively to help characterize fluid-filled porous materials. The method provides several advantages compared to other techniques. NMR is non-invasive and generally does not require the use of doping to separate the fluid signal from the matrix, as is needed with X-ray computed tomography (CT) measurements. It provides advantages compared to optical spectroscopy techniques, such as Fourier transform infrared spectroscopy (FTIR) or Raman, as it can be used to characterize opaque samples. NMR is also a flexible analytical method; by using different pulse sequences, many different sample properties can be evaluated in the same equipment setup. As such, NMR has been used to measure a wide range of information on fluid-filled porous media, such as porosity [1], permeability [2–4], fluid typing [5–8], and wettability [9–12]. One of the most common uses for NMR in porous materials is as a measure of the pore size distribution in the sample [13–15].

Low-viscosity fluids, such as water, brine, and light oils, have both long transverse and longitudinal relaxation times, generally on the order of a few seconds. When these fluids are placed inside a porous material, the fluid molecules encounter the pore surfaces, which enhance their relaxation rates [16]. For longitudinal relaxation, this is described by the equation

$$\frac{1}{T_1} = \frac{1}{T_{1bulk}} + \rho_1 \frac{S}{V}, \quad (1)$$

where  $T_1$  is the measured longitudinal relaxation time;  $T_{1bulk}$  is the bulk relaxation time of the saturating fluid; the surface relaxivity,  $\rho_1$ , describes how efficient the surface is in enhancing the longitudinal relaxation rate;  $S$  is the surface area of the pore, and  $V$  is the pore volume. Small pores have a large surface-to-volume ratio, such that the molecules will encounter the pore surface more frequently, and the pore will have a faster relaxation rate. Conversely, large pores have a small surface to volume ratio, such that the molecules encounter the pore surface less frequently, and the pore has a slower relaxation rate. For low-viscosity liquids, it can be assumed that the bulk term is negligible and the equation can be simplified to the following:

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$$\frac{1}{T_1} = \rho_1 \frac{S}{V}. \quad (2)$$

The relationship for transverse relaxation in a porous material is similar to that of the longitudinal relaxation [17]:

$$\frac{1}{T_2} = \frac{1}{T_{2bulk}} + \rho_2 \frac{S}{V} + \frac{D\gamma^2 G^2 \tau_e^2}{12}, \quad (3)$$

where  $T_2$  is the measured transverse relaxation time;  $T_{2bulk}$  is the bulk relaxation time of the saturating fluid; the surface relaxivity,  $\rho_2$ , describes how efficient the surface is in enhancing the transverse relaxation rate;  $D$  is the diffusion coefficient of the spin-bearing molecule;  $\gamma$  is the gyromagnetic ratio;  $G$  is the strength of the magnetic field gradient; and  $\tau_e$  is the echo spacing. This third term in the equation arises because, in addition to the influence from pore size, the measured  $T_2$  is also affected by the diffusion of the fluid molecules in magnetic field gradients. These magnetic field gradients can be intentionally applied, as is the case for measuring molecular diffusion or imaging, or they can arise naturally as internal gradients that occur resulting from the magnetic susceptibility differences between the solid matrix and saturating fluid. While internal gradients can be used to provide information on the porous system [11,18], frequently, they are considered a hindrance and their effect on the measurement is sought to be minimized. Provided the transverse relaxation is measured using a short echo time and the internal gradients are relatively weak, their effect can be ignored such that the transverse relaxation equation can also be simplified for low-viscosity fluids:

$$\frac{1}{T_2} = \rho_2 \frac{S}{V}. \quad (4)$$

For Eqs. (1)–(4) to be valid and, thus, for the NMR relaxation distributions to accurately reflect the pore size distribution, the system needs to be in the fast diffusion limit [13]. Here, fluid molecules frequently sample the surface within a pore, but exchange between pores is slow. In this situation, a single pore will produce a single relaxation time. Then, when the signal from all of the different pores is measured, the resulting distribution of relaxation times will reflect the pore sizes present in the sample.

One of the major drawbacks of using NMR to measure pore size is that the results are only a relative distribution. To obtain an absolute pore size distribution, surface relaxivity needs to be known. Unless this is known *a priori*, which is usually not the case, further experimental measurements will be required. If another absolute measure of pore size needs to be performed to calibrate the NMR results, performing NMR in the first place to calculate pore sizes can seem extraneous. To avoid running further experimental measurements, rules of thumb are sometimes applied to provide a quick estimate of the expected pore size distribution based on the sample composition. For example, sandstone is typically assumed to have a surface relaxivity of 3  $\mu\text{m/s}$ . In reality, the value of surface relaxivity of sandstone can vary over orders of magnitude [19].

The most commonly used method for determining surface relaxivity is correlation of NMR data to mercury injection capillary pressure (MICP) measurements [20]. This method measures pore sizes in a sample by forcing mercury into it at different pressures and recording the amount of mercury that will enter for a given entry pressure. The surface relaxivity values for  $T_1$  and  $T_2$  are then determined by converting the relaxation data into a pore size using Eqs. (2) and (4), respectively, and determining the value that produces the best overlap with the MICP curves. While MICP measures the pore throat size and NMR measures the pore body size, there is generally a correspondence between these two values in sandstones, though this does not always hold true. Other methods that can be used to obtain pore size distributions to calibrate NMR data

are thin sections [21,22], X-ray CT measurements [23,24], Bruauer–Emmett–Teller (BET) [25] or NMR diffusion [26,27] methods. Measuring relaxation on samples that have been dried until only a monolayer of surface water remains has also been used to estimate surface relaxivity in porous samples [28,29].

Despite the need for calibration, NMR has been well established for logging in both petroleum [30–32] and water resource [33–35] applications. Here, NMR is used to make continuous measurements of relaxation time along the length of a borehole, sometimes over thousands of meters. Then, for calibration, samples of rock from the borehole are sent to a laboratory, where NMR measurements and a measure of pore size distribution are both made, most commonly MICP. These results are used to estimate the surface relaxivity, which can then be applied to the NMR logs to provide an estimate of pore size. However, only a few samples, typically a dozen or less, are used to provide a calibration for the length of the well. Furthermore, sample size and condition are other limitations of the method. A sufficiently large sample is needed to make a reliable NMR measurement, and this often necessitates taking core from the borehole, which is a slow and expensive undertaking, to calibrate logging data. Cuttings or small bits of leftover rock from the drilling process cannot easily be used for log calibration. The accuracy of NMR measurements on cuttings is a significant concern, as keeping the samples saturated but removing any excess surface fluid for measurement is a challenge. In the case of polycarbide diamond bits, the rock is frequently reduced to a fine powder, such that the pore structure is obliterated and application of NMR and MICP are not possible.

While calibration is typically performed empirically, the mechanism behind surface relaxivity in sandstones is well established [36–41]. Throughout the pore surface, there exist paramagnetic impurities. When fluid molecules encounter these impurities, the coupling between the electron and nuclear spins will serve to quickly relax the NMR signal of the molecule. Because in the fast diffusion limit all of the fluid molecules are expected to explore the pore space on the time scale of the NMR measurement, the pore fluid provides a single relaxation rate. This also means that the distribution of the impurities is unimportant; only their concentration is significant [36]. Some studies have found approximately linear increases in the surface relaxivity with paramagnetic concentration [37], while others simply found monotonic increases [39,40].

Numerous studies have been performed to understand the effect of paramagnetic ion content on the relaxation rate in sandstones [36–41]. However, these studies have had one common drawback: they were performed on artificial samples. The samples were created using precise mixtures of known constituents. This provides good control over a single variable at a time, allowing thorough investigation of its effect on surface relaxivity. However, real samples can contain multiple types of paramagnetic species, and creating artificial mixtures that can fully cover the variable space of different possible elements that might affect surface relaxivity would be an onerous undertaking.

This study takes another approach to determining surface relaxivity. Instead of creating artificial samples with a known fraction of paramagnetic material, relating the content of paramagnetic species in natural sandstones to their surface relaxivities is attempted. LIBS is increasingly adopted for measuring elemental content [42,43]. This method uses a high-power laser to ablate a small portion of material. The amount of sample that is ablated by the laser is typically on the order of a few nanograms, such that the technique is generally considered nondestructive. The material is turned into high-temperature plasma, which emits light at characteristic elemental wavelengths as the plasma cools. The intensity of the peaks can be related to the concentration of the elements in the sample. Because of different elemental emissivity coefficients, peak

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