Low Frequency EPR and EMR Point Spectroscopy and Imaging of a Surface

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Abstract

Low frequency electron paramagnetic resonance (LFEPR) spectrometers operating between 100 and 500 MHz typically have large-volume magnets that accommodate large samples. LFEPR spectroscopy with a 2.9 mm diameter surface coil was used to record point spectra and image the spatial distribution of the spin probe 2,2-Diphenyl-1-picrylhydrazyl (DPPH) and electrophotographic toner in printed letters on a flat surface. The location of the surface coil was fixed on the desired location when a spectrum was recorded. The magnetic field of the spectrometer was fixed on the location of the signal and the sample was scanned under the surface coil in parallel trajectories to produce an image of the signal in the letters "LFEPR". We speculate on the utility of this technique to study flat objects such as paintings and illuminated manuscripts with cultural heritage significance.

Key Words: Low frequency electron paramagnetic resonance, LFEPR, electron paramagnetic resonance, EPR, electron magnetic resonance, EMR, surface imaging, toner, DPPH

Introduction

Electron paramagnetic resonance (EPR) and electron magnetic resonance (EMR) spectroscopies are commonly performed at Larmor frequencies (ν) at or above 9 GHz and restricted to samples of a few mm^3 in volume. Examination of large, intact ($> 10 \text{ cm}$) objects with EPR spectroscopy is challenging owing to the limitations of cavity resonators used for providing the oscillating magnetic field (B_1) at the Larmor frequency to the sample and the small space between the poles of the magnet producing the applied magnetic field (B_0). A 9 GHz EPR design that has the potential to examine larger, intact objects has been reported, [1] however it was developed to examine smaller, near-microscopic ($600 \mu\text{m}^3$) objects.

Low frequency electron paramagnetic resonance (LFEPR) spectrometers typically operate at $100 < \nu < 500 \text{ MHz}$ and can accommodate samples which are several liters in volume.[2-5] The ability to accommodate large samples is attributed to the large volume magnetic field [3-5] and the lower operating frequency of LFEPR spectrometers compared to conventional 9 GHz EPR spectrometers. The lower operating frequency makes the construction of surface coils and creation of large volume sample probes simpler.

LFEPR spectroscopy also avoids microwave heating of tissues associated with 9 GHz EPR and can therefore be used in whole animal or human studies. [4,5] This paper focuses on a materials application of LFEPR, although the techniques we present may have applicability *in vivo* studies.

EPR has been used to study objects with cultural heritage significance by destructively or invasively removing a small part of a large object and placing it in a spectrometer.[6-11] LFEPR, however, can be used to study large objects with cultural heritage significance non-invasively and non-destructively.[2] In this paper we address the utility of LFEPR to study flat

objects containing paramagnetic or ferri/ferromagnetic pigments by demonstrating the ability of LFEPR to both record point spectra and image the spatial distribution of the stable free radical 2,2-Diphenyl-1-picrylhydrazyl (DPPH) and electrophotographic toner. Several electrophotographic toners contain ferri/ferromagnetic nanoparticles.[12,13] The EMR g factor of these nanoparticles tends to be smaller than for atomic ions and molecular radicals as the magnetic domains are larger. The g factor for toner is approximately 1.85, [13] while that for molecular radicals and ionic atoms is greater than two.

Materials and Methods

We used the laboratory built continuous wave LFEPR spectrometer with magnetic field modulation and phase sensitive detection at 10 kHz described previously.[2,3] The field modulation was provided by a 15 cm inside diameter (ID) Helmholtz coil driven by a Techtron 7570 audio frequency amplifier. The sample resonator was a 2.9 mm ID inductively coupled surface coil (SC) consisting of a closely wound, five-turn solenoid of #26 enameled copper wire and a 5 pF chip capacitor. The SC had a resonance frequency (ν) of 271.46 MHz and a quality factor (Q) of 75. When the surface coil is placed against a surface, its radio frequency magnetic field (B_1) is perpendicular to the surface. The SC was fixed in the center of the 30 cm ID solenoidal electromagnet such that B_1 was perpendicular to the B_0 magnetic field from the electromagnet. B_0 could be swept or fixed at any value between 0 and 18.7 mT. For surface spectroscopy or imaging, the sample is located on an acrylic sample stage that was moved under the SC with a two axis positioning system located outside the magnet.

The sensitivity map of the surface coil defines the sample volume for point spectroscopy and the best point spread function (PSF) achievable for surface imaging. An approximate

relative sensitivity map of the surface coil in a plane perpendicular to the circular edge of the coil and passing through the diameter was measured and is presented in Fig. 1. The sensitivity was mapped by moving a 1.5 mm diameter, 0.25 mm thick disc of DPPH in epoxy by 0.02 mm steps using a two-axis micrometer.

Rotating the two-dimensional sensitivity map about the SC axis gives an approximation of the three-dimensional sensitivity map ($S(x,y,z)$) for the SC. The SC sensitivity drops off with distance from the coil center. In general, the sensitive region of the SC can be thought of as spherical cap on the bottom of the coil. If 0.34 is arbitrarily chosen as the minimum, useful, relative signal value, a 3.8 mm^3 sensitive volume for the coil is defined by a spherical cap of height 0.75 mm, radius 2.25 mm, and base radius 1.75 mm. When the SC is placed on a sample with a concentration distribution of spins, $C(x,y,z)$, the EPR signal is proportional to the volume integral of the product of $C(x,y,z)$ and $S(x,y,z)$.

$$EPR \text{ Signal} \propto \iiint C(x,y,z) S(x,y,z) dx dy dz \quad (1)$$

In the limit of infinitely thin samples, the volume integral becomes an area integral and the sensitive region becomes a circular disc.

It should be noted that the sensitivity map of Fig. 1. only approximates the PSF owing to the finite size of the DPPH disc used to create the sensitivity map. For a 0.25 mm thick surface sample, the PSF as a function of radial position (r) of the coil is approximately

$$PSF = -0.136r^2 - 0.187r + 0.998 \quad (2)$$

Two samples were used to test the performance of the point spectroscopy and surface imaging capabilities of the system. The first was DPPH, which has a single $g=2.0036$ peak in the EPR spectrum. This sample was prepared by mixing DPPH (Sigma-Aldrich) in epoxy (Loctite, 5 min) and stenciling #72 Arial font (18.3 mm high) letters LFEPR in a 0.2 ± 0.05 mm

thick layer on a sheet of vinyl. (See Fig. 2.) Note that these stenciled letters are not perfect: the letters F and E have a slight tilt to the left, and there are discontinuities where the bowl of the P and R attach to the stem due to filling the gap created by the bridge supporting the island in the letters' bowl with epoxy/DPPH.

The electrophotographic toner sample was a piece of 75 g/m^2 weight, 92 bright, white recycled copy paper (Staples[®] 620016) with the letters LFEPR printed on it in #72 Arial font by a Hewlett-Packard[®] (HP) LaserJet 1200 printer using OfficeMax[®] toner formulated for this HP printer. The EMR linewidth (Γ) of ferri/ferromagnetic nanoparticles is dependent on the size and shape of the nanoparticle, as well as interparticle interactions. [14,15] The 9.1 GHz EMR spectrum of HP toner has a $g \approx 1.85$, $\Gamma \approx 110 \text{ mT}$ absorption.[13] This Γ value is greater than the $B_0 = 10.47 \text{ mT}$ value for $g = 1.85$ at $\nu = 271 \text{ MHz}$, as well as the sweep width on our instrument.

Results

Spectra from a point in each sample were obtained by centering the probe on the stem of the letter L. Fig. 3a shows the LFEPR spectra of DPPH in epoxy and for the paper. The LFEPR spectrum of toner fused to paper has the characteristic feature displayed in Fig. 3b. The signal increases from a minimum at $B_0 = 0$ as B_0 is increased, similar to that seen for some ferromagnetic nanoparticles at 9.5 GHz. [16] In the absence of toner on the paper, the signal is equal to the background noise of the instrument.

For mapping the spatial distribution of DPPH and toner in our text samples, the magnetic field was fixed at the value B_F indicated by the vertical lines in Fig. 3., and the LFEPR spectrometer set to constantly record signal at a rate of 5 points/s with an RC time constant of 0.1 s. The sample was moved at 1 mm/s so as to acquire signal along n parallel trajectories running

the length of the sample and separated by Δ . The n subsequent signal versus distance spectra were processed with a linear baseline correction, then combined to form a $561 \times n$ element matrix. No additional processing was performed on this matrix to form the image composed of $0.2 \times \Delta$ mm pixels. The B_F , n , and Δ values for DPPH and toner were respectively 9.55 mT, 30, 1 mm and 7.5 mT, 17, 2 mm. As there is no peak in the EMR spectrum of toner on paper, we arbitrarily choose $B_F = 7.5$ mT, where the signal-to-noise ratio equals 10, to record the signal. Fig. 4 displays the 561×30 pixel image for DPPH (a) and the 561×17 pixel image for toner (b).

Discussion

Figure 3 demonstrated that the SC, positioning system, and LFEPR spectrometer can be used to record an EPR point spectrum of a stable free radical and the smaller EMR signal from electrophotographic toner fused to the surface of a sheet of paper. Our current LFEPR spectrometer can accommodate a 15 cm wide, 3 m long flat object. The former limit is set by the modulation coil diameter while the latter is set by the room dimensions. The spatial resolution is limited by the diameter of the SC and the spatial sampling. Spectral resolution is limited by the typical EPR spectral parameters such as B_0 homogeneity and modulation amplitude. We believe this ability will allow us to place large flat objects such as illuminated manuscripts and paintings in our magnet and identify the composition of a pigment based on its EPR spectrum. The spectrometer may also be able to distinguish between pigments with similar colors but different EPR spectral features, as was demonstrated previously in a single turn solenoid volume resonator for Han, Egyptian, and ultramarine blue pigments.[2]

Owing to the 3.5 mm diameter of the sensitive region under the SC, both text samples were oversampled in the length direction at 5 pts/mm. The Δ increment between the scan lines was 1 mm for DPPH and 2 mm for toner. The large Δ for toner was chosen for expediency and to

determine the effect of the large value on quality. Some detail was lost in the text quality but the letters were clearly visible. The quality of the displayed images could have been improved by interpolating in the n direction to achieve square pixels, but this was not performed so as to give a true representation of the capabilities of the technique. Note that the stenciling process did not produce a uniform distribution of DPPH in the letters, and that the letters F and E were at a slight angle. The imaging was able to pick up this slight angle in the two letters.

Conclusions

Our results demonstrate the utility of LFEPR with a small diameter surface coil to measure the spatial distribution of an EPR or EMR signal-containing material on a large flat surface. This result cannot be achieved with conventional, high frequency EPR spectrometers which utilize iron core magnets with narrow pole gaps as it is extremely difficult to satisfy the resonance condition of B_1 perpendicular to B_0 with this geometry. With the larger air core electromagnets found on LFEPR spectrometers it is easier to satisfy the resonance condition and perform raster based surface imaging with a small surface coil. Our results open up the possibility of spectral imaging of multiple components in a painting or illuminated manuscript by either choosing B_0 values corresponding to different spectral peaks or scanning an entire LFEPR spectrum for a grid of locations in the sample.

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Figure Captions

- Fig. 1. The measured EPR sensitivity map for a plane perpendicular to the bottom the coil. The two circles indicate the position of the bottom winding of the surface coil.
- Fig. 2. Images of the DPPH in epoxy stenciled on vinyl (top), and electrophotographic toner fused to paper (bottom).
- Fig. 3. The LFEPR spectra of a) DPPH in epoxy, and b) electrophotographic toner on paper and paper without toner. Vertical line indicates the signal at the B_0 value used to scan the images in Fig. 2.
- Fig. 4. An LFEPR image of the #72 font letters LFEPR stenciled in epoxy with DPPH on a sheet of vinyl (top), and electrophotographically printed toner on paper (bottom). The images were obtained by rastering the flat sample under a small surface coil probe while keeping B_0 fixed at respectively 9.55 and 7.5 mT.

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4

LFEP R

LFEP R