

## Measurement of Free-Radical Concentration in Solids by Electron Paramagnetic Resonance Comparison Technique

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### Synopsis

A brief theoretical background of free-radical concentration measurement by electron paramagnetic resonance (EPR) comparison technique is presented to clarify the criteria required for the measurement. Simple experimental methods are suggested to improve the accuracy of the measurement by taking into account the effects of rf power saturation and instrument parameters on the spectral records.

### INTRODUCTION

In concept, the measurement of free-radical or unpaired electron-spin concentration seems straightforward. However, Hyde<sup>1</sup> states that "of all the measurements one can make with an epr equipment, the determination of absolute spin concentration is the most difficult." He presented two alternative measurement procedures, an absolute and a comparison technique. In the first, the unknown spin concentration is calculated from the spectrometer parameters and from the relationship between the spin concentration and the magnetic susceptibility. In the second, the unknown is measured relative to a standard reference such as DPPH (1,1-diphenyl-2-picrylhydrazyl with one unpaired spin per molecule) or other calibrated substances having a long-term stable spin concentration.<sup>2</sup> Hyde<sup>1</sup> also states that the comparison technique usually has justified preference. In this technique, the unknown spin concentration is calculated from the ratio of the area under the two EPR absorption lines recorded from the reference and from the unknown samples at identical thermal, electronic, rf power, and d.c. field conditions. Validity of the calculation is based on the assumption that the two records are the true absorption lines and neither of the two samples is saturated by the rf power applied. Since the measurement is difficult, and the theoretical back ground for the measurement is deeply implicated in the general theory of magnetic resonance,<sup>3-5</sup> the need to prove the existence of nonsaturation is generally overlooked or misunderstood.<sup>6a</sup> Bloch equations<sup>5</sup> show, however, that rf saturation may have a serious adverse effect on the accuracy of the measurement. For these reasons the first objective of this paper is to present a brief theoretical

background of spin concentration measurement by the comparison technique. The second is to suggest experimental methods for finding the true absorption line and the rf powers for nonsaturation and to show that the effect of rf power saturation always must be taken into account in the calculation of the spin concentration.

### THEORETICAL BACKGROUND

When a paramagnetic substance is placed in a d.c. magnetic field and thermal equilibrium is reached, the static magnetization is proportional to the field intensity  $H$ . The proportionality factor is the static mass susceptibility<sup>5</sup>  $X_0$ . The unpaired electron spins (elementary paramagnets) align with their moments either parallel or antiparallel to the direction of  $H$ . The relationship between  $X_0$  and the spin concentration  $N$  depends on the nature of the spin species and how the energy levels of the spins in the magnetic field are populated thermally. If the spin population of the energy levels are at their Boltzmann values, then, for stable unpaired spins,  $X_0$  is given by the familiar Curie's law expression<sup>5</sup> which gives  $X_0$  as proportional to  $N$ . The proportionality factor depends on the absolute temperature of the substance. Curie's law is valid if the excited states of the unpaired spins for the applied magnetic field are not multiple states. When an rf magnetic field with an angular frequency  $\omega$  of resonance for  $H$  is applied perpendicular to  $H$ , the response of the magnetization is proportional to the rf field intensity  $H_1$ , provided that the rf field does not change the Boltzmann distribution of the spins, i.e., no rf saturation of the spin population in the excited states occurs. The proportionality factor includes  $X_0$ . Portis<sup>7</sup> showed that the Kramers-Kronig relations are applicable for the magnetic susceptibilities of an electron spin system if the energy levels are not saturated. If a magnetic resonance absorption line in the absence of saturation satisfies the Bloch equations<sup>8</sup> modified for a linearly polarized field, then  $X_0$  is proportional to the integral of  $X''(\omega)$ , the absorption part of the total susceptibility of the spin system,<sup>4</sup> where  $\omega$  is an absorption frequency about  $\omega_1$ , the center frequency of the absorption line, and  $X''(\omega)$  is related to the actual rf power  $P_a$ , absorbed by the spin system as  $X''(\omega) = P_a/2H_1^2\omega_1$ . Moreover, when saturation is absent  $X''(\omega)$  is not a function of  $H_1$  and, since  $\omega = \gamma H$ , the integral for  $X_0$  will be

$$X_0 = \frac{\gamma}{\pi\omega_1^2 H_1^2} \int_{-\infty}^{+\infty} P_a dH, \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio. Equation (1) states that when the energy levels of the spin system are not saturated,  $X_0$  is proportional to the area  $A$  under the absorption line yielded by the absorbed rf power  $P_a$  as a function of the d.c. magnetic field intensity  $H$ . In other words, the invariance of  $X_0$  to a change in the rf power is adequate proof that the spin system is not saturated. Cummerow and Holliday<sup>10</sup> showed that the absorption line of paramagnetic resonance is the plot of the rf power absorbed

by the paramagnetic system against the d.c. magnetic field intensity at resonance.

Equation (1) complies with the experimental procedure of an adiabatic, slow sweep of the d.c. magnetic field through resonance at a fixed frequency  $\omega_1$ , so that  $dH/dt \ll \gamma(\Delta H)^2$  and  $\Delta H \gg H_m$ , where  $\Delta H$  is the line width and  $H_m$  is the amplitude of  $\omega_m$ , the audio frequency modulation of the d.c. field, both in field units.<sup>2,4</sup>  $H_m$  must be selected so that  $\omega_m$  is smaller than the reciprocal of the spin-spin relaxation time and so that the modulation index  $\beta = \gamma H_m / \omega_m$  is very small (from 0.1 to 1). The RC time constant of the lock-in amplifier also should be matched to the rate of d.c. field sweep. Then the lock-in amplifier output is the differential of the true absorption line.<sup>11</sup> Further, eq. (1) also implies that there is no skin effect.

Crucial points in determining the spin concentration  $N$  are that the static susceptibility  $X_0$  is independent of the rf power if the spin system is not saturated, and that  $X_0$  and not  $N$  is obtained directly from the measurement.<sup>3</sup> Since Curie's law is valid for any number of unpaired electron spins existing at the same time in a molecule,  $N$  may represent the number of free-radical sites or, with a change in the proportionality factor, the number density of paramagnetic molecules.<sup>3</sup>

### EXPERIMENTAL TECHNIQUE

In the comparison technique, the unknown spin concentration  $N_u$  in a sample  $u$  is determined relative to the known spin concentration  $N_r$  in a reference sample  $r$ . It is often possible to provide a reference sample so that the gyromagnetic ratio for the two samples are approximately equal and that neither of them is saturated by an rf power,  $P_0$ , fed to the cavity resonator; then  $P_a$  in eq. (1) is proportional<sup>12</sup> to  $P_0$ . If the true absorption lines for the two samples with identical filling factors are recorded at this  $P_0$  and under the same thermal, electronic, and d.c. field conditions, then the unknown spin concentration is given from Curie's law and eq. (1) as

$$N_u = N_r \frac{A_{u0} M_r}{A_{r0} M_u} \quad (2)$$

where  $A_{u0}$  and  $A_{r0}$  are the areas under the absorption line and  $M_u$  and  $M_r$  are the mass of samples  $u$  and  $r$ , respectively. It is evident from the published experimental techniques, and from the above theory,<sup>2,4,13</sup> that the true absorption line for the samples may be obtained by changing either of the parameters  $dH/dt$ ,  $RC$ ,  $H_m$ , and  $\omega_m$ , until the change produces an increase in the signal intensity and a decrease in  $\Delta H$ , while  $H_m$  times amplifier gain, the temperature, and the rf power are fixed.

For samples with very low spin concentration, which start to saturate at very low rf power,<sup>14</sup>  $A_{u0}$  may not be measured accurately either because of the low sensitivity of the detection system or the small sample volume applicable, or both. If  $A_{us}$  and  $A_{rs}$  are the areas under the absorption lines

for samples  $u$  and  $r$  recorded at an rf power  $P_s$  fed to the cavity, which saturates the spin systems, then  $N_u$  is given from eq. (2) as

$$N_u = N_r \frac{A_{us}\delta_{rs}M_r}{A_{rs}\delta_{us}M_u} \quad (3)$$

where  $\delta_{us}$  and  $\delta_{rs}$  are the saturation indices at  $P_s$  for samples  $u$  and  $r$ , respectively. The saturation index is defined here as

$$\delta_s = \frac{D_s}{D_0} \quad (4)$$

where  $D_s = A_s/P_s$  and  $D_0 = A_0/P_0$ , and  $A_s$  and  $A_0$  are the areas under the absorption line at  $P_s$  and  $P_0$ , respectively. The definition is based on Curie's law and eq. (1) which implicitly state that, when the rf power level  $P_s$  is sufficiently high to disturb the Boltzmann distribution of the spins, then  $P_s$  is not proportional to  $P_a$ , but rather shows saturation.<sup>15</sup> Equation (3) shows that, to calculate  $N_u$  from the spectral records, both  $\delta_{us}$  and  $\delta_{rs}$  have to be known. For a fixed  $P_s$ , the values of  $\delta_{us}$  and  $\delta_{rs}$  can be read from saturation curves. Figure 1 shows the saturation curves for free radicals in polycrystalline DPPH, sucrose charpyrolyzed at 500°C, periodate lignin chars at 500°, 300°, and 200°C, and UV-irradiated cellulose and dioxane lignin as the plot of  $\delta_s$  versus  $P_s$ . All these samples were measured under vacuum. Curve D, however, was obtained by placing sample E in oxygen at 25°C and 1 atm for an indefinite time. The figure shows that, at saturation,  $\delta_s$  decreases with an increase in  $P_s$ . This is expected from eq. (4), the propor-

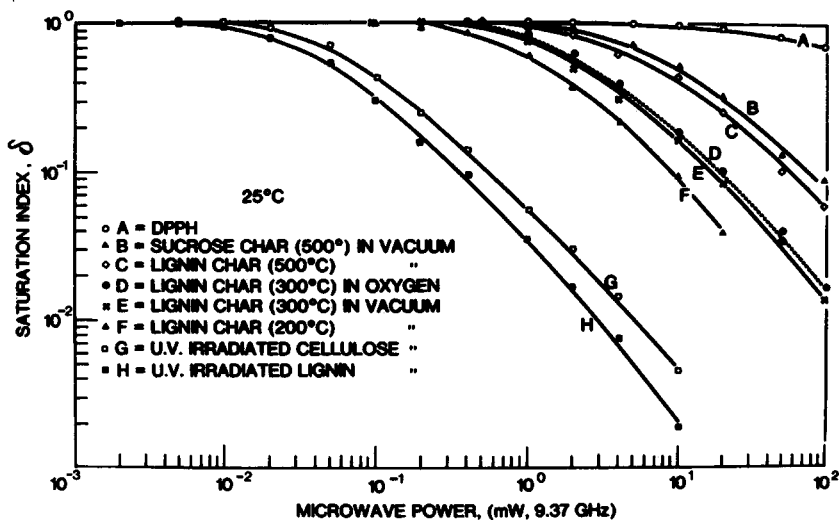


Fig. 1. Saturation curves for free radicals in polycrystalline DPPH (A), sucrose charpyrolyzed at 500°C (B), lignin chars at 500°C (C), 300°C (D and E) and 200°C (F) and uv-irradiated cellulose (G) and lignin (H) as the plot of  $\delta_s$  vs.  $P_s$ . All these samples are under vacuum. Curve D is obtained by placing sample E in oxygen at 25°C and 1 atm.

tionality of  $P_s$  to  $H_1$ , and the Bloch equation<sup>5</sup> for  $X''(\omega)$ . The shift of curve E to curve D indicates that oxygen has reduced the extent of rf saturation.

The saturation curves were obtained from EPR spectra recorded by a spectrometer described elsewhere.<sup>16</sup> The method of recording the spectra was as follows. With each sample several absorption spectra were recorded at various  $P_s$  values in the range from 1  $\mu$ W to 100 mW into the cavity (TE 102, X-band), while the other electronic, field, and thermal conditions were fixed. When  $P_s$  was changed, the v-mode rf power unbalance in the bridge detection head was adjusted to the same fixed value. The crystal detector was operated in the square-law conversion region and the cavity at optimum coupling.<sup>12</sup>

Equation (3) indicates that the saturation indices of an unknown and a reference may be neglected without appreciable error if they are approximately equal. Figure 1 shows that at negligible saturation, the saturation index for any sample is approximately equal to unity. So at negligible saturation of the two samples,  $\delta_{us}$  and  $\delta_{rs}$  may be neglected. However, as curves A and H in Figure 1 and eq. (3) show, a measurement of spin concentration (in irradiated lignin with respect to DPPH at several milliwatts), without taking into account the saturation indices, can result in an error of a few orders of magnitude.

The experimental procedure of plotting for the saturation curves seems rather laborious. It is clear, however, that spin concentration cannot be measured without ensuring that the rf power applied does not cause saturation, and the saturation curves give the valid information for that. For symmetric lines with inhomogeneous broadening, however, the area under the absorption line is proportional to the maximum signal height<sup>7,17</sup>  $f_m$ . If the spectrometer is not suitable for finding  $P_0$  and  $A_0$ , or  $f_{0m}$  at nonsaturation, then a curve as a plot of  $A_s/P_sM$  or, for inhomogeneous broadening,  $f_{sm}/P_sM$  versus  $P_s$  may be used, where  $M$  is the mass of the sample. Equation (4) and Figure 1 show that at a  $P_s$ , a very small slope of the curve, which decreases with a decrease in  $P_s$ , indicates negligible saturation. However, a large slope for sample  $u$  approximately equal to that for sample  $r$  does not necessarily mean that  $\delta_{us} = \delta_{rs}$ .

## CONCLUSIONS

The theoretical background and the experimental technique presented indicate that when the free-radical concentration is measured by an EPR comparison technique, the saturation indices for the reference and the unknown samples always have to be included in the calculation [eq. (3)]. This method greatly improves the accuracy of the data at the expense of a more extended measurement procedure. The time of measurement, however, can be reduced appreciably if reference samples of free radicals with long-term stability are selected and their saturation curves are available. This more elaborate method differs from that given by Lockhart and Jones<sup>6a</sup> for finding the maximum value of the rf power which does not saturate the spin

system. It is evident from the Bloch equations<sup>8</sup> and this study, however, that their method produces rather the optimum value of the rf saturation than the maximum value of nonsaturation.<sup>6b</sup>

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