Carbon-Based Standards for Electron Paramagnetic Resonance Spectroscopy

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Abstract. In order to meet the need for a good new EPR intensity and g-value standard whose paramagnetic species are carbon-based radicals, several materials were investigated, including coal, fusinite (a coal maceral), and several carbohydrate chars. Of the prototypical standards prepared, a chemically-treated fusinite is recommended as most suitable because of its chemical stability, spin density, EPR signal line shape and line width, microwave power saturation characteristics, availability, and homogeneity. Effects of dilution with KBr, KCl, and polymer are negligible, although the line width is broadened in the presence of paramagnetic gases. Several model standard compounds have been prepared in a polymer matrix to minimize changes in packing density over time.

1. Introduction

There is a great need for standards in electron paramagnetic resonance (EPR) spectroscopy. In a survey completed last year by the International Society for EPR Spectroscopy (ISEPRS), every respondent (n = 130) stated that the need for standard samples was great, and that scientists would be eager to acquire standards if they were available. While the exact number of EPR spectrometers in the world is somewhat uncertain, owing to the large number of instruments constructed by individual scientists from components, the number of functioning commercial spectrometers is about 7000. The ISEPRS has enrolled almost 2000 members in the first year of existence, drawing from those spectroscopists most active in research, and estimates that this represents about 10% of the active research workers in the field. Another rapidly growing group of EPR users exists in industries where the spectroscopy is employed in testing, quality control, process control, and
other routine measurement tasks. Japanese industries lead the world in this area of applied EPR spectroscopy, and representatives developing and using such industrial applications also express the need for reliable, easy-to-use standard samples. Rapid growth of this non-research sector of EPR spectroscopic applications is now occurring. For example, the advent of widespread use of EPR techniques in radiation dosimetry is dramatically increasing commercial demand for EPR instrumentation and EPR standards.

The unusual circumstance of a widely utilized spectroscopic technique without recognized and accepted standard samples is partly a historical accident. Instrumentation sales to the EPR community was for many years dominated by Varian Associates, an electronics firm that held patents on the klystron tube, and that marketed the first commercial EPR instruments in the late 1950's. Varian developed standard samples for calibration and performance evaluation of its spectrometers, and these were so carefully formulated, so stable, and so well-calibrated, that they became de facto standard reference materials for the field. About 5000 copies of the Varian standards, called Varian Weak Pitch and Varian Strong Pitch, were sold between 1958 and 1984. Most were sold at the time of a spectrometer sale, but since these standards were sealed in 5 mm quartz glass tubes, they frequently were broken, and a brisk sale of standard samples always took place. In 1984, Varian left the EPR business, and with their exit, the supply of Varian standard samples stopped. Steady loss of samples through breakage over the last nine years has virtually eliminated this once widely accepted standard from the field.

Varian based its standard materials on a free radical-containing tar obtained from the Reilly Tar Corporation. This choice was particularly fortuitous, since standards formulated from this starting material met almost all the criteria for ideal standard materials. These include:

1. Chemical stability and purity (or homogeneity).
2. Ease of manufacture (grinding, accurate dilution, etc.).
3. Single, isotropic spectral line at g = 2.
4. Spectral line width ($\Delta B_{pp}$) $\approx$ 5 Gauss.
5. Ideal line shape (Gaussian or Lorentzian).
6. Moderate saturation behavior ($P_{1/2} > 10$ mW).

Varian samples did well at fulfilling all but requirements #2 and #5. They were not particularly easy to make. Pitch tar was ground in a ball mill with KBr to achieve the desired dilution, then the powder was placed in a 4 mm o.d. quartz tube and evacuated for several days. The sample was compacted to achieve uniform packing density, then sealed in the glass tube and calibrated. EPR line shapes in such standards were broader in the wings than Lorentzian.