A Simple and Convenient EPR Standard for Determination of *g*-Factors and Spin Concentrations

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The commercially available cement Picein 80 has been tested and successfully used for the determination of g-factors and spin concentrations at X- and Q-band frequencies. The main advantages compared to other standards are a very small space requirement and the fact that the concentration of the standard can be easily adjusted to the signal intensities of the sample. This standard exhibits a single line at a *g*-factor of 2.0041 with a halfwidth of .47 mT and a spin concentration of 2.10^{15} spins/mg Picein. An additional weaker resonance occurs at $g = 2.0177$, and at Q-band a partly overlapping multiplet with 5.8 mT separation is observable, but the intensities of both signals are low compared to that of the main signal. This standard is applicable over the whole range of useful spin concentrations, and the linewidth makes it particularly useful for measurements on transition metal ions in diluted single crystals.

Introduction

Detailed descriptions of intensity and *g*-factor standards for EPR work may be found in several textbooks [1–3]. However, these standards are subject to at least one of the following disadvantages:

a) Higher linewidths than for most paramagnetic centers at low concentrations (crystalline transition metal compounds). With these standards accuracy in the determination of *g*-factors is low and errors of the concentration measurements may result from largely different ratios of modulation amplitude and halfwidths.

b) Instability against storage, light and/or oxygen atmosphere (DPPH, F-centers in alkali halides, charred dextrose [4, 5], tetracene positive ions [6]).

c) Anisotropy due to fine structure at higher microwave frequencies or need for exact alignment of anisotropic crystals (DPPH [5]), ruby [7]) are time consuming and/or cause loss of accuracy.

In addition almost all standards need extra space and may necessitate use of special accessories like a dual cavity. Space limitation is most stringent at higher microwave frequencies where direct frequency measurements are still a largely unsolved problem. Also, many standard samples are limited in their application to a certain concentration range and require preparation of different probes for largely varying concentration ranges.

We successfully tested and used Picein 80 (K. Roth, D-7500 Karlsruhe), a thermoplastic cement for high vacuum equipment. It is commercially available at a low price, stable in air over a wide range of temperatures, easily adjustable to the concentration of paramagnetic centers in the sample and can be applied as cement between sample and sample holder or at the sample container in the sample position with little space requirement.

Properties of the Standard

The most prominent signal of Picein 80 is a single line with a *g*-factor of 2.0041 ± 0.0001, a halfwidth of 0.47 mT and a shape between Gaussian and Lorentzian. An additional weaker signal (less than 4% amplitude of the main line) appears at $g = 2.0177$ at X-band with a halfwidth of 1 mT (see Figure 1). At Q-band an additional, partly overlapping multiplet with 6 mT separation and 1 mT halfwidth occurs at a slightly higher field than the main signal with 5% amplitude of the main signal (see Figure 2). The main signal is saturable at 4 K, the spin-lattice relaxation time T_1 at 4 K was determined by the continuous saturation method [9] with $T_2 = 7 \cdot 10^{-9}$ sec determined from the linewidth. A value of $T_1 = 2 \cdot 10^{-5}$ sec was obtained.

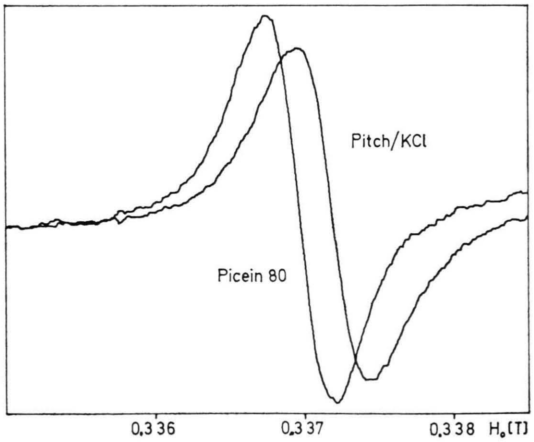

Fig. 1. EPR spectra of Picein 80 and pitch in KCl at X-band (9.452 GHz).

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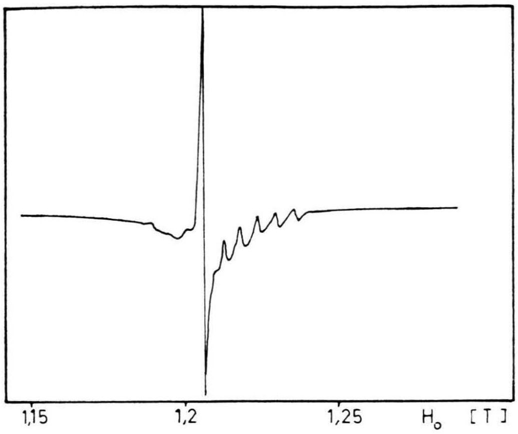

Fig. 2. EPR spectrum of Picein 80 at Q-band (33.96 GHz).

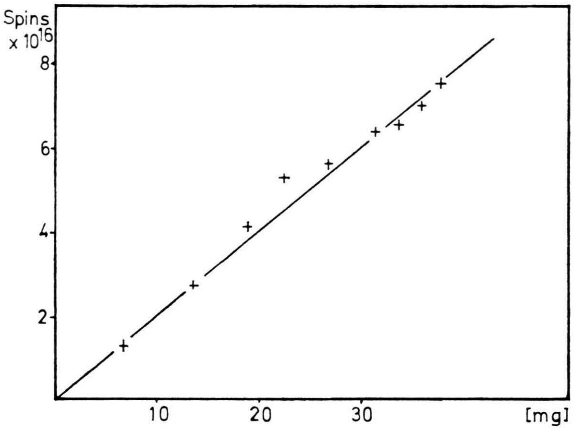

Fig. 3. Determination of the spin concentration for the main signal in Picein 80 at X-band with pitch in KCl as standard.

The concentration of free spins represented by the main signal was determined against pitch in KCl. From the calibration curve in Fig. 3 a value of $(1.97 \pm 0.10) \cdot 10^{15}$ spins/mg Picein 80 was obtained at X-band, at Q-band the standard deviation was 60% higher, most likely due to larger errors in the weight determination for masses up to 10 mg.

Some Remarks on the Use of this Standard

For sample signals of comparable halfwidths and g-factors between 2.001 and 2.007 overlapping complicates simultaneous registration of sample and reference signals. Even at these limits the apparent g-factors in the composite signal are wrong by about 0.0001 leading to a systematic error of twice this magnitude, and the apparent halfwidths in the derivative spectra are almost 20% too small. More accurate values can be obtained by curve resolution since the individual signals can be recorded separately. This standard appears to be particularly well suited for transition metal ions in diamagnetic crystals which normally have similar halfwidths, but effective g-factors sufficiently different from the free ion value.

Higher accuracies in the mass determination for low spin concentrations can be achieved if a solution of Picein in benzene (or acetone) of known concentration is prepared and a measured volume of this solution is evaporated on the sample or sample container. In this way the range of usable spin concentrations can be extended to the detection limit. No change in signal intensity was observed with solution and subsequent evaporation of the benzene. The signal of a benzene solution has the same characteristics as that of the solid except that at Q-band it is completely symmetrical whereas that of solid Picein always exhibited some asymmetry (compare Fig. 2), even if the Picein was applied as a very thin layer.

If in a simultaneous measurement the assignment of the signals to sample and standard is dubious, the spectrum can be remeasured with an increased amount of Picein. Regardless whether the Picein is used as cement between sample and sample holder or applied as a layer on the sample or sample container, the additional space requirement for this standard is always negligible. Also differences in the magnetic field at sample and standard can be avoided in this way.

Acknowledgements

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