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Description of the EPR Spectrometer at the Department of Chemistry and Biochemistry.

Bruker EMX-6/1 X-band EPR spectrometer composed of:
- EMX-113 console
- ER-041-XG X-band microwave bridge with built-in microwave frequency counter
- ER-070 6 inch magnet with 60 mm air gap (0-6400 Gauss, but note that the Hall field meter only works in the 100-16000 Gauss range!)
- EMX-080 1 kWatt magnet power supply
- EMX-032 Hall field probe with electronics for interfacing with the magnet
- ESR-900 or ER-4112-HV Oxford Instruments variable temperature helium flow cryostat (3.8-300 K).

Cavities were used with a finger dewar for measurements at liquid nitrogen (77K) or with the above flow cryostat fitted to the cavity.

Cavities:
- ER-4119-HS, high sensitivity perpendicular-mode cavity (serial no. 0315)
- ER-4116-DM, a dual-mode cavity (serial no. 0301)

Data acquisition was with the software supplied by Bruker (WINEPR Acquisition program, May 1, 1997, version 2.3.1.), data manipulation (determination of g-values, subtraction, baselining, integration and conversion to ASCII files for use with Origin or Microsoft EXCEL) was done with the WINEPR program version 2.11.

EPR tubes (Wilmad, 714-PQ-8) were 4 mm outer diameter (0.38 mm wall thickness) and 13.5 cm length, high purity quartz tubes.

The samples were stored in the dark immersed in liquid nitrogen. To facilitate handling, the EPR probes were linked with a pierced rubber tubing to polystyrene sticks with a label on it.

Notes on Optimizing Sensitivity: Instrumental Factors

Minimize microphonics. The high Q of the microwave cavity makes the system susceptible to microphonic generated noise. Vibration of the sample within the cavity may modulate the mode patterns, frequency, and Q of the microwave cavity. Depending on the nature and frequency of the microphonics (the power spectrum of the noise), these vibrations may generate noise spikes or contribute to the white noise. *Prevent microphonic noise pick-up by securing the waveguide with the waveguide stabilizers.* Secure the sample in the cavity by tightening the collets on the cavity sample stack to hold the sample rigidly in place. Do not place objects on the microwave bridge or the magnet table that may vibrate or are free to move. Avoid placing a frequency counter with a fan on top of the bridge.

Maintain a controlled environment for the best spectrometer performance. Air drafts past the spectrometer, especially the cavity, may induce temperature fluctuations or microphonics from sample vibration. Large fluctuations in the ambient temperature may degrade performance by reducing the frequency stability of the cavity. Very humid environments may cause water condensation when you are cooling your sample with a variable temperature system. Condensation inside the cavity may be reduced by maintaining a constant purging stream of dry nitrogen gas. *Note that excessive gas flow rates may generate microphonic noise through sample vibration.*

Minimize electrical interference. Noise pick-up from electromagnetic interference (EMI noise) may be encountered in some environments. It may be possible to reduce EMI noise by shielding or perhaps by turning the noise source off if generated by equipment near the spectrometer.

Periodically check the iris coupling screw for tightness of fit. A worn iris screw thread will make the iris susceptible to microphonics which can modulate the cavity coupling.

The sample to be investigated should be inserted in the cavity and tuned according to the spectrometer manual. This adjustment should be made for all experiments limited by signal to noise considerations. The optimum AFC modulation depth is a function of the loaded cavity Q. Consequently, slight variations in the optimum setting may be anticipated. If you are using a finger dewar with a boiling refrigerant such as liquid nitrogen, you should turn the AFC modulation level to maximum.

Insert a cryostat in the cavity. Quartz has a dielectric constant of 3.8 but a low dielectric loss. Insertion of high purity quartz sleeves, such as the variable temperature dewar, actually concentrates the microwave magnetic field intensity at the sample. The increased field intensity produces an EPR signal that has a larger signal to noise ratio than is achieved in the absence of the dewar insert. *Experiments limited by the signal to noise ratio may benefit by the use of the variable temperature quartz insert dewar, even if the experiment is run at room temperature.*