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Thin Cylindrical Sample Positioning In/Out Of the Centre of a Bruker Rectangular Cavity

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Abstract

The response of the microwave cavity to the correct (in the cavity centre) *versus* incorrect (out of the cavity centre) positioning of an "over full-length cavity", thin cylindrical sample in the Bruker single TE_{102} rectangular microwave cavity has been analysed. It was concluded that when the sample approaches the "front-back" cavity walls (which corresponds to a shift of the sample centre along the cavity z-axis, Δz), a significant decrease in EPR signal intensity (*Ipp*) was observed, whereas when the sample approaches the "right-left" cavity walls (which corresponds to a sample shift along cavity y-axis, Δy), a significant increase in the *Ipp* values was found. Therefore, accurate and precise positioning of each thin cylindrical sample tube, which is filled with powder material or frozen solutions, in the microwave cavity is the principal, necessary and imperative condition in EPR spectroscopy. A special alignment procedure for the accurate and precise positioning of such thin cylindrical samples in the microwave cavity is essential in EPR practice.

Keywords: EPR spectroscopy, sample positioning, thin cylindrical tube, microwave cavity

Introduction

A multitude of sources of error influence the accuracy and reproducibility of EPR experiments (see elsewhere (Hyde 1962, Kohnlein, 1963, Yordanov and Ivanova 1994, Casteleijn et al. 1968)). The list of instrumental- and sample- associated variables, which can affect each EPR measurement, is very extensive (Waren and Fitzgerald 1977), and the majority of these errors occur simultaneously and synergistically. As has been clearly shown in the literature (for Varian (Casteleijn et al. 1968, Barklie and Sealy 1992, Nagy and Placek 1992, 1994) and likewise for Bruker (Mazur et al. 1996a, 1997a, 2000, 2001, 2006) rectangular cavities), the most important primary error source in the EPR measurements is the positioning of the samples within the microwave cavity. Variation in these parameters could cause significant errors in the primary phase of EPR experiment (i.e., data acquisition). The systematic studies of the above-mentioned topic have been reported only for a point-like sample (Casteleijn et al. 1968, Nagy and Placek 1992, 1994, Mazur et al. 2000). In the present contribution, the response to the correct (in the cavity centre) *vs.* incorrect (out of the cavity centre) positioning of a thin cylindrical sample in the Bruker microwave cavity is analysed. The corresponding errors in EPR measurements caused by such variation in thin cylindrical sample position are discussed. The main aim of this paper is to give useful recommendations how to minimize the influence of such primary error sources in EPR spectroscopy.

Experimental

The "over full-length cavity", thin cylindrical samples of internal diameter, *i.d.* = 1.5 mm, length, L = 30 mm, and wall thickness of the quartz sample tube, $\delta \approx$ 0.1 mm, (strong pitch in KCl) were prepared and EPR signal intensity values were measured according to the previous papers (Mazur et al. 1996a, 1997a, 2000, 2001) of this series. The X-band (≈ 9.4 GHz) EPR spectra were recorded using a field-modulated Bruker EMX EPR spectrometer with the original single TE_{102} (ER 4102 ST) rectangular cavity (Bruker Analytical Messtechnik and Instruments 1983, 1998). In all cases, the intensity of the EPR signal was characterized by the peak-to-peak height of the first-derivative EPR signal, *Ipp*. Statistical evaluation of the obtained data was carried out according to standard procedures.

The "over full-length cavity", thin cylindrical samples were concentrically positioned along the common sample cavity x-axis (the cavity and sample centre were coincident), and the samples were then shifted along the cavity *z*- or *y*- axis. The sample centre was always localised in the central, horizontal (*y*, *z*) plane of the rectangular cavity. The EPR spectra were recorded and analysed for each sample position in the cavity. The different positions of the thin cylindrical sample in the microwave cavity are illustrated in Fig. 1. Further details about the original sample alignment procedure for precision positioning and shifting of the cylindrical samples in the rectangular cavity are given in our previous papers (Mazur et al. 1996b, 1997b, 2000, 2001, 2006).

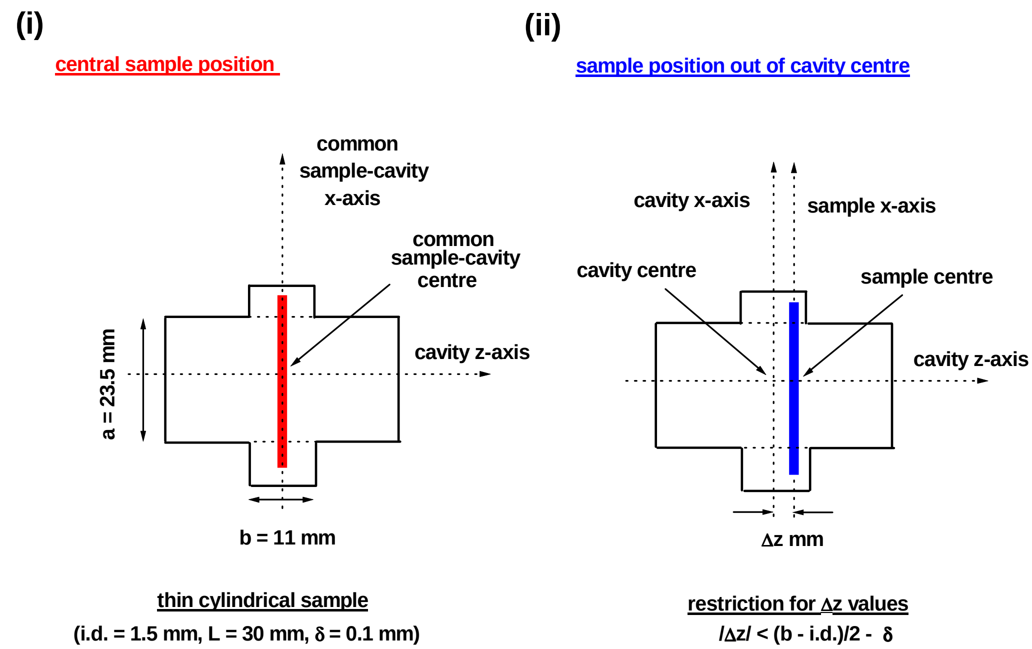

Fig. 1. Schematic diagram of "over full-length cavity", thin cylindrical sample positioned in a Bruker single TE_{102} rectangular cavity. The view is along the *y*-axis, which is parallel to the B_0 field axis and perpendicular to the sample *x*-axis. The sample centre is always in the central, horizontal (*y*, *z*) plane of the rectangular cavity. Two situations are shown, which correspond to: (i) the correct, central sample position, and (ii) the incorrect sample position, in which the sample centre was shifted out of the cavity centre along the z-axis by Δz.

Results and Discussion

In the previous parts of this series (Mazur et al. 1996a, 1997a, 2000), the response of the microwave cavity to the shift of the point-like sample out of the cavity centre along the *x*-, *y*-, and *z*- axis of the single TE_{102} and double TE_{104} rectangular cavities was investigated. Consequently, the response of the cavity to the shift of the thin cylindrical samples out of the cavity centre along the *y*- and *z*- axis of the Bruker single TE_{102} rectangular cavity has been analysed. The source of errors that is caused by such variably positioned samples is discussed and recommendations for diminishing such errors are given.

Figure 2 shows how the change of the normalized experimentally observed peak-to-peak height of the first-derivative EPR signal, ΔIpp [%], varies with the shift of the centre of the thin cylindrical sample (*i.d.* = 1.5 mm, *L* = 30 mm, and $\delta \approx 0.1$ mm) along the *z*-axis, Δz,

(= ±1.25, ±2.25, ±3.25, and ±4.25 mm) out of the centre of the single TE_{102} rectangular cavity. The averaged values are from five independent measurements. The averaged *Ipp* value of the thin cylindrical sample concentrically positioned along the common sample-cavity *x*-axis (Δz = 0) was taken as 100 %.

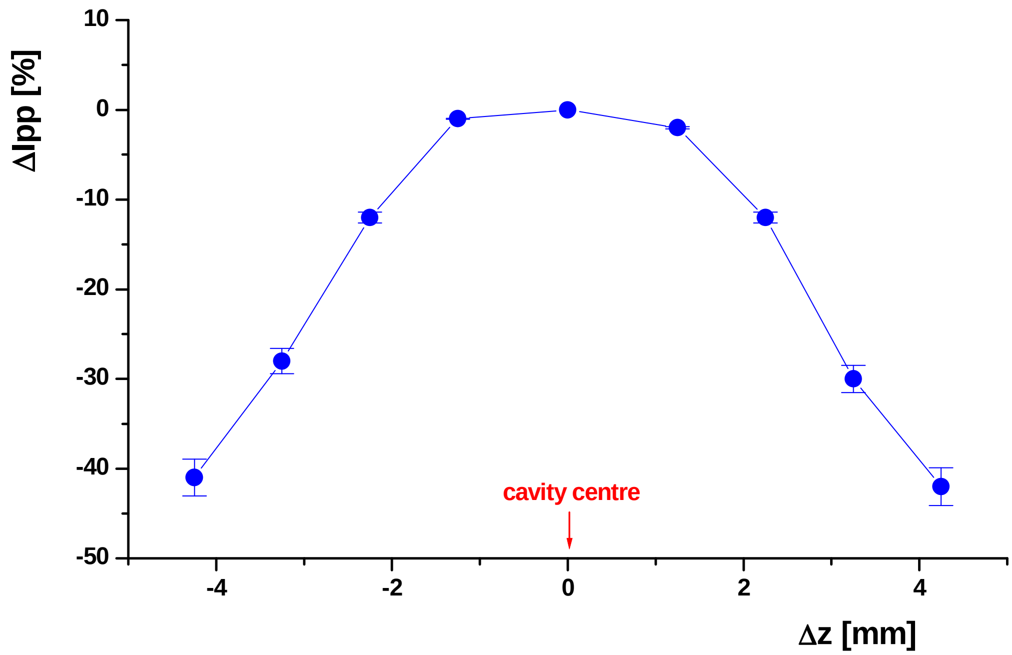

Fig. 2. Variation of the change of the normalised experimentally observed peak-to-peak height of the first-derivative EPR signal, ΔIpp [%], on the shift of the sample centre along the cavity *z*-axis, Δz, out of the centre of the single TE_{102} rectangular cavity. The averaged values are from five independent measurements. The averaged *Ipp* value of the correct, concentrically positioned thin cylindrical sample was postulated to be 100 %.

From Fig. 2 the following can be concluded:

(a) The shift of the sample centre out of the cavity centre along the z-axis (“front-to-back” axis of cavity) always *decreased* the *Ipp* values compared to the sample position in which the cavity and sample centre are coincident.

(b) For a sample centre shift out of the cavity centre along the cavity z-axis with, Δz = ±1.25 mm, the ΔIpp values changed very slightly, i.e., the *Ipp* values in this sample position decreased less than 3 % compared to those of a concentrically positioned sample.

(c) For the sample centre shift with, $\Delta z = \pm 2.25$ mm, the *Ipp* values decreased ca 15 % compared to the *Ipp* value of the sample positioned in the cavity centre.

(d) For $\Delta z = \pm 3.25$ mm and ±4.25 mm, the *Ipp* values further decreased about 30 % and up to 40 % compared to the *Ipp* value of the sample in the central cavity position.

Figure 3 shows how the change of the normalized experimentally observed peak-to-peak height of the first-derivative EPR signal, *ΔIpp* [%], varies with the shift of the centre of the thin cylindrical sample along the *y*-axis, *Δy*, (= ±1.25, ±2.25, ±3.25, and ±4.25 mm) out of the centre of the single TE_{102} rectangular cavity. The averaged values are from five independent measurements. Again, the averaged *Ipp* value of the thin cylindrical sample concentrically positioned along the common sample-cavity x-axis ($\Delta y = 0$) was taken as 100 %.

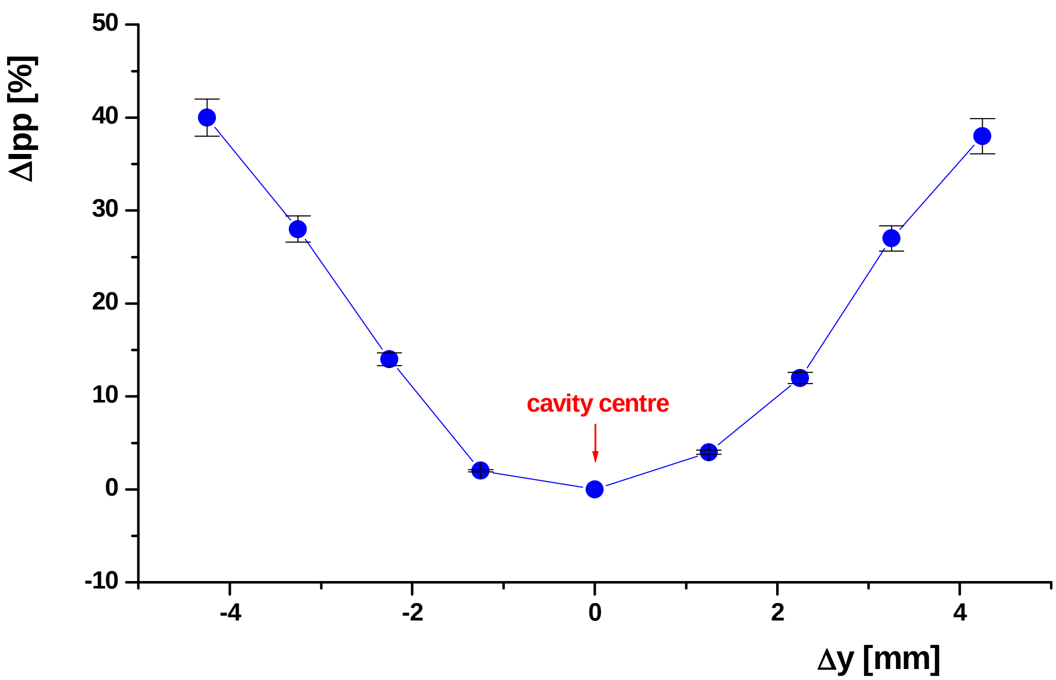

Fig. 3. Variation of the change of the normalised experimentally observed peak-to-peak height of the first-derivative EPR signal, *ΔIpp* [%], on the shift of the sample centre along the cavity y-axis, *Δy*, out of the centre of the single TE_{102} rectangular cavity. The averaged values are from five independent measurements. The averaged *Ipp* value of the correct, concentrically positioned thin cylindrical sample was postulated to be 100 %.

From Fig. 3 the following can be concluded:

(a) In contrast to the above-mentioned results, a shift of the sample centre out of the cavity centre along the *y*-axis (“left-to-right” axis of cavity) always *increased* the *Ipp* values compared to the sample position in which the cavity and sample centre are coincident.

(b) For the sample centre shift out of the cavity centre along cavity y-axis with, $\Delta y = \pm 1.25$ mm, the ΔIpp values changed very slightly, i.e., the *Ipp* values in this sample position increased less than 3 % compared to those of concentrically positioned sample.

(c) For the sample centre shift with, $\Delta y = \pm 2.25$ mm, the *Ipp* values increased ca 15 % compared to the *Ipp* value of the sample positioned in the cavity centre.

(d) For $\Delta y = \pm 3.25$ mm and ± 4.25 mm, the *Ipp* values further increased about 30 % and up to 40 % compared to the sample in the central cavity position.

It is obvious that the trend of the experimentally obtained dependences in Fig. 2 and Fig. 3 is very similar in the absolute value of the ΔIpp changes, but the shift of the sample centre out of the cavity centre along *z*- or *y*- axis of the microwave cavity exhibits the opposite effect, i.e., a *decrease* and *increase* of the *Ipp* values, respectively. This trend is in a good accord with literature data obtained for a point-like sample in the Varian single rectangular cavities (Casteleijn et al., 1968, Nagy and Placek 1992, 1994) and with our previous observations for a point-like sample in the Bruker single TE_{102} and double TE_{104} rectangular cavities (Mazur et al. 2000), in that when the sample approaches the “front-back” cavity walls (which corresponds to a shift of the sample centre along the cavity *z*-axis, Δz), a significant *decrease* in *Ipp* values was observed, whereas when the sample approaches the “right-left” cavity walls (which corresponds to a sample shift along cavity *y*-axis, Δy), a significant *increase* in the *Ipp* was found. It is generally accepted that these unusual *Ipp* dependences were due to the high non-uniformity of the modulation field produced by the pair of Helmholz coils, which are mounted in the left- and right- walls of the microwave cavity (Casteleijn et al. 1968, Nagy and Placek 1992, 1994, Mazur et al. 2000).

In conclusion, all the above-mentioned phenomena constitute source of significant errors in EPR measurements. This is the case even if samples of identical material, volume, and shape are being compared, but are differently positioned inside the microwave cavity. Therefore, the following are recommendations for the positioning of thin cylindrical samples that are to be compared in each EPR studies:

(a) Accurate and precise positioning of each thin cylindrical sample tube, which is filled with powder material or frozen solutions, in the microwave cavity is the principal, necessary and imperative condition in EPR spectroscopy.
(b) A special alignment procedure for the accurate and precise positioning of thin cylindrical samples in the microwave cavity is essential in EPR measurements.
(c) The sample centre should be coincident with the centre of the cavity. We believe that these tips will be helpful in EPR practice.

Acknowledgement

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