

X-Band Two-Channel EPR Spectrometer for Simultaneous Registration of Signals of Two Samples

1. Introduction

In EPR spectrometry the need of quantitative measurements often becomes obscured to specify of the spin quantity in the tested sample. Quantitative measurements usually are very difficult to take out since the intensity of a watched EPR signal depends not only on spin quantity in a tested sample but it depends also on many other factors, e.g. microwave power level in the sample, resonator Q-factor (with a sample), modulation level of the magnetic field, resonator volume to sample volume ratio and gain of the receiving path. Because the quantitative specification of some of these factors is very difficult, so in order to avoid of this problem comparative measurements in respect to reference samples are most often applied. But in practice it is very difficult (and sometimes impossible) to ensure the property of the reference sample enough close to the property of the sample under test – it especially refers to cases, in which both samples are of different volume and size. In the result the both samples are being measured in various conditions. It is possible to ensure similar conditions of the measurement only during simultaneous registration of EPR signals coming from both samples, placed in the same resonator [1].

On the other hand, wanting to account exactly of the spectroscopic g ratio, it is possible to add the special pattern sample to the tested sample or to determine of the microwave frequency and the value of the magnetic field exactly in the place of the tested sample. The first method is most often applied - however the unfavourable phenomenon is putting on oneself of the spectra of the both sample signals (of the pattern sample and of the tested sample). In general it is very difficult to introduce a pattern sample into the tested sample. In the other cases the extra equipment is needed: the microwave frequency meter and the NMR magnetic field meter.

All of these problems are to avoid in an EPR spectrometer system equipped with double resonator (two chamber cavity) and with double measuring and receiving system, making simultaneous recording of signals coming from two samples. The idea of such a spectrometer is known and is characterised in basic manuals referring to the EPR spectrometry technique [1.2] - however it is very rarely applied. Such a system is a combination of nearly two spectrometers, working at the same time with the single, double resonator. None of commercial companies offers such a spectrometer in principle. In the year 1982 [3.4] the Varian X-Band EPR spectrometer equipped with low frequency receiver for Q-Band was rebuilt for the spectrometer making simultaneous recording of the signal of two samples in the X-Band. This solution made it possible to carry quantitative measurements and the measurement of the g ratio out with a high accuracy.

The pulse EPR spectrometers eliminate partially mentioned above problems however in many cases EPR spectrometers of continuous wave (CW) are not to replace.

Simultaneous recording of two EPR signals is possible in the spectrometer fitted with the special, double resonator - making it possible to put two different samples and fitted with two independent modulation-receiving paths – enabling suitable modulation levels and suitable gain values for signals coming from both of samples. In order to avoid of unwanted interference between two signals, the frequencies of both modulating signals should differ from themselves considerably – the frequencies of 100kHz and 1kHz are a good choice. The computer system, enabling simultaneous recording of two EPR signals is necessary, of course.

2. X-Band 2-channel EPR spectrometer

The concept as well as the full configuration of X-Band 2-channel EPR spectrometer is shown in Fig. 1 and 2. In comparison to an ordinary CW EPR spectrometer, the 2-channel EPR spectrometer is fitted with two independent signal receivers, with double resonator and with special computer system enabling simultaneous recording of two different signals coming from two different samples. The full 2-channel EPR spectrometer may be built as an advanced upgrade of an older type EPR spectrometer (Radiopan, Varian, Bruker, Jeol etc.) – the following old units as field controller,

signal receiver and cavity have to be replaced with new units. For a such purpose the new, researched in Wrocław University of Technology fully computer controlled EPR spectrometer units as digital field controller, digital signal receiver for 1kHz and 100kHz, double resonator and special computer control program are assigned [5-9].

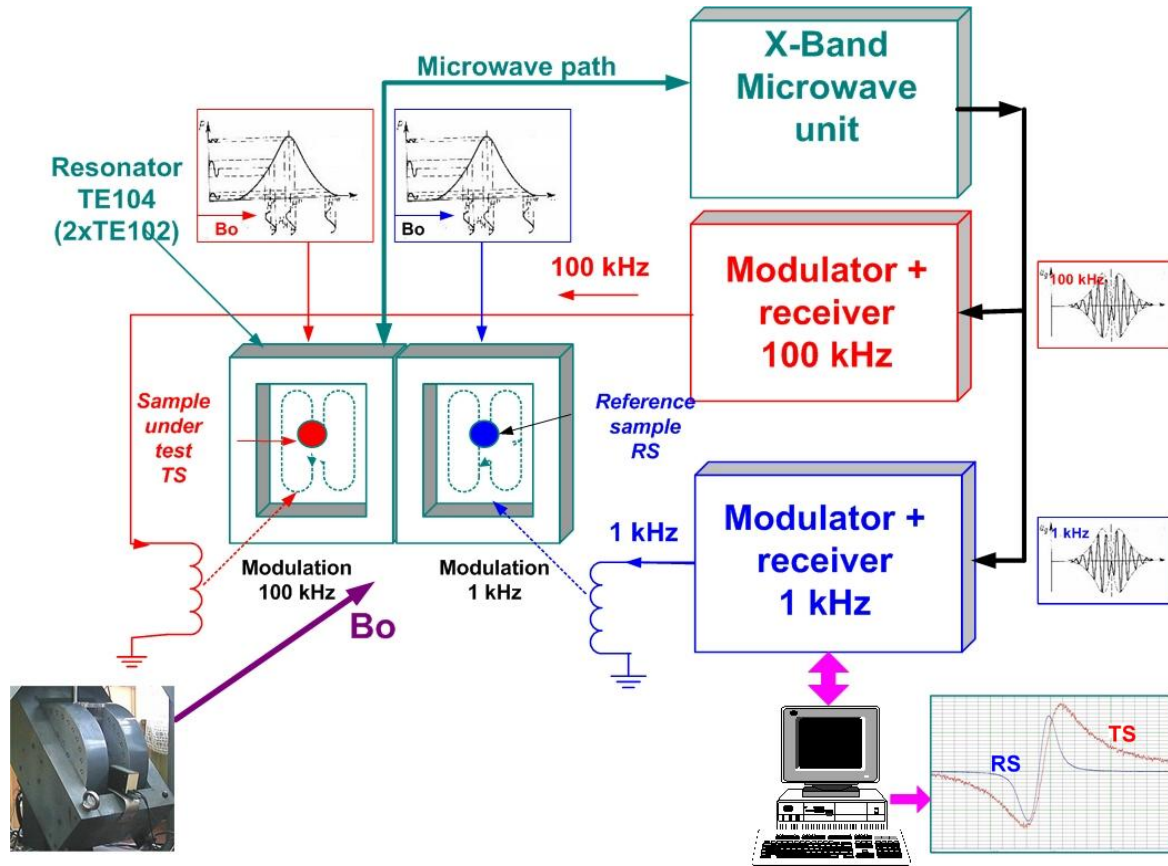


Fig. 1. Concept of 2-channel EPR spectrometer with simultaneous recording of two EPR signals

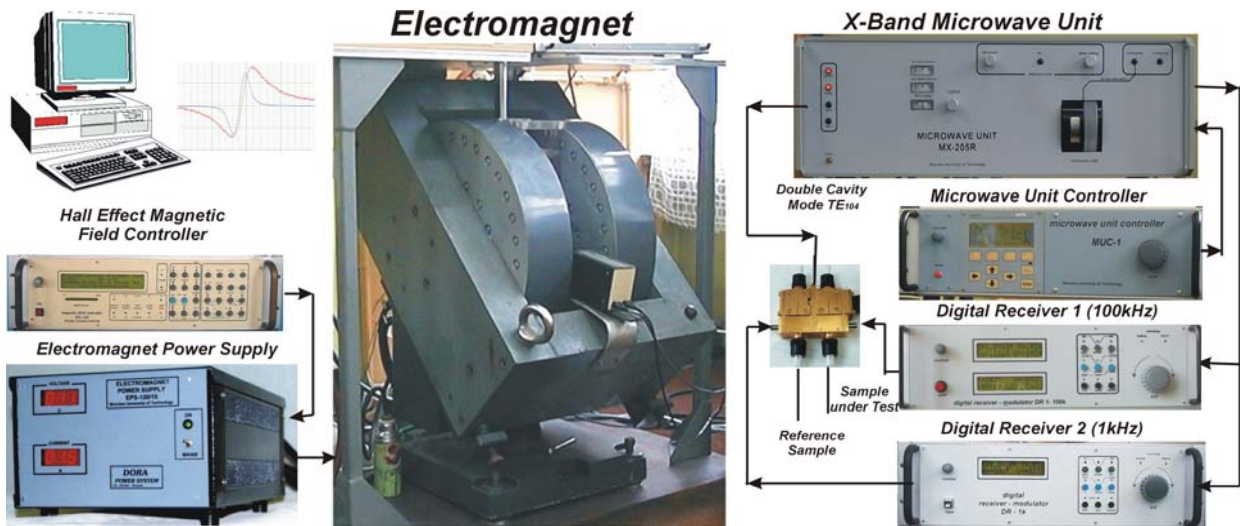


Fig. 2. Configuration of X-Band 2-channel EPR spectrometer

A such advanced upgrade of “Radiopan” EPR spectrometers has been made in Medical Academy in Bydgoszcz and in University (Department of Physics) of Białystok – both in Poland. The new units (in 19” cabinets) have been placed in spectrometer console after removing of old units (together with X-Y recorder). The view of the upgraded spectrometer is shown in Fig. 3.

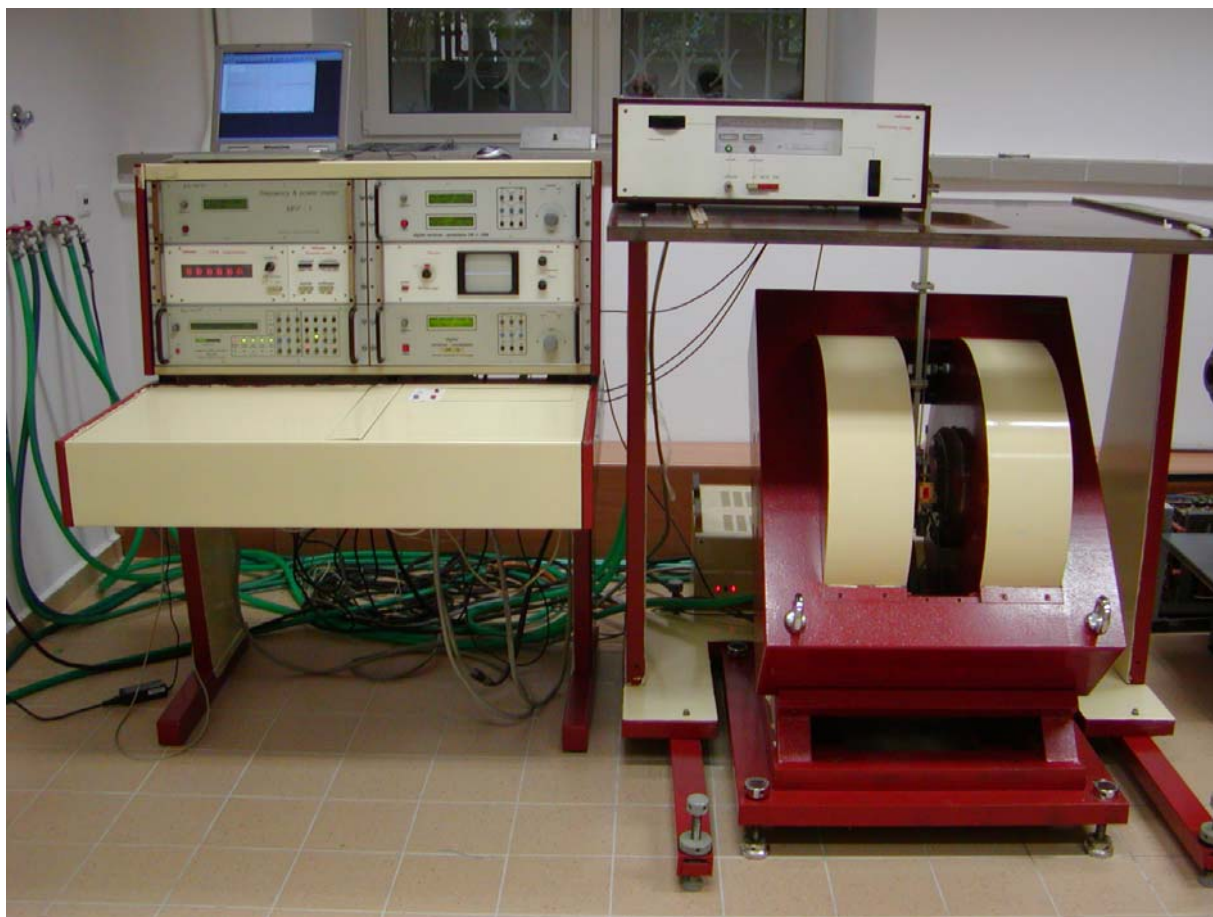


Fig. 3. View of 2-Channel X-Band EPR spectrometer in Białystok

3. Double resonator with TE104 mode

A double resonator with the TE104 mode is necessary for 2-channel EPR spectrometer. The double resonator with the TE104 mode has been made by putting together (with its narrower sides) of two identical rectangular resonators with the TE102 mode – Fig. 4. Rectangular resonators of “Radiopan” as well as of Wrocław University of Technology are suitable for this purpose. Here is very important condition that both resonators must be maximally similar. Since both signal paths are independent of oneself and they are able to be separately used, so the double resonator is also to be used for standard single measurements.

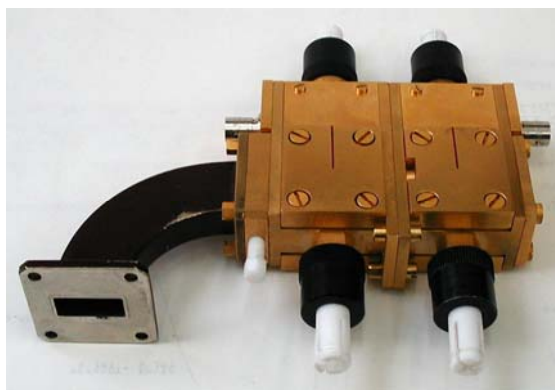


Fig. 4. Double resonator with the TE104 mode

4. Computer control program

A special computer program to control of the 2-channel EPR spectrometer via USB interface has been designed. The main window and edition window of the program are shown in Fig. 5 and 6.

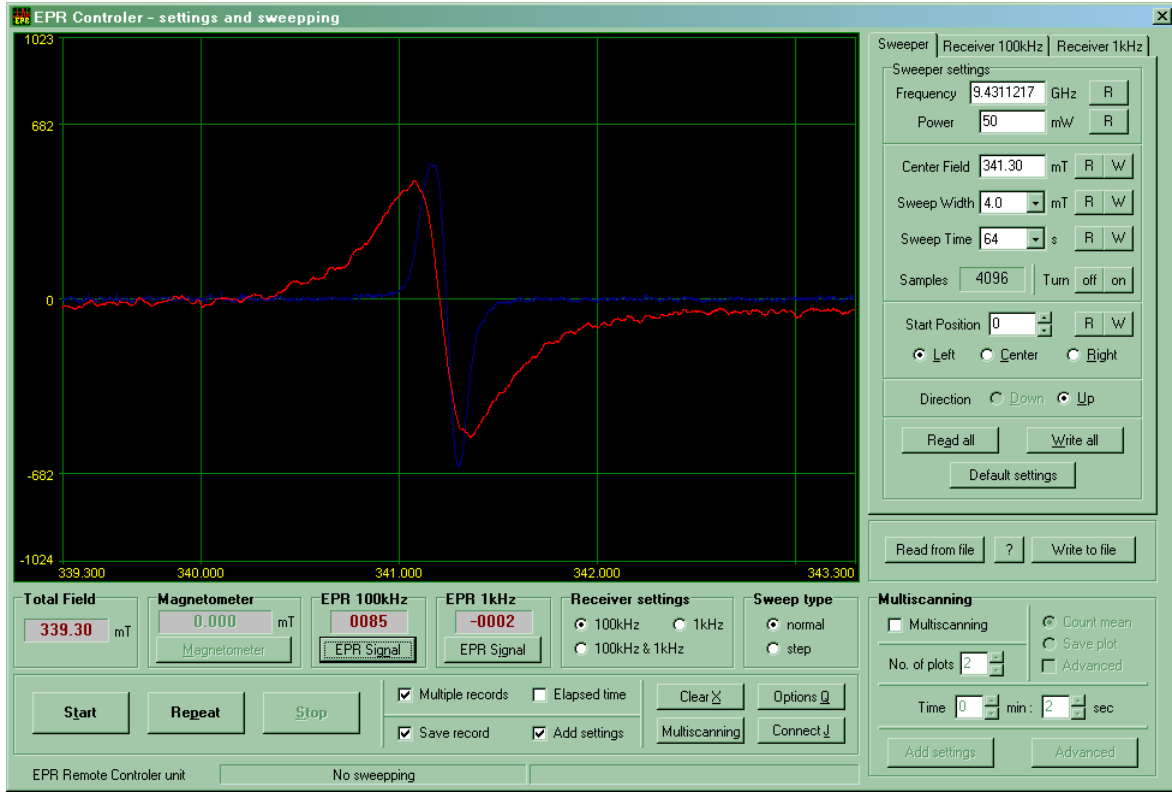


Fig. 5. Main window view of the control program

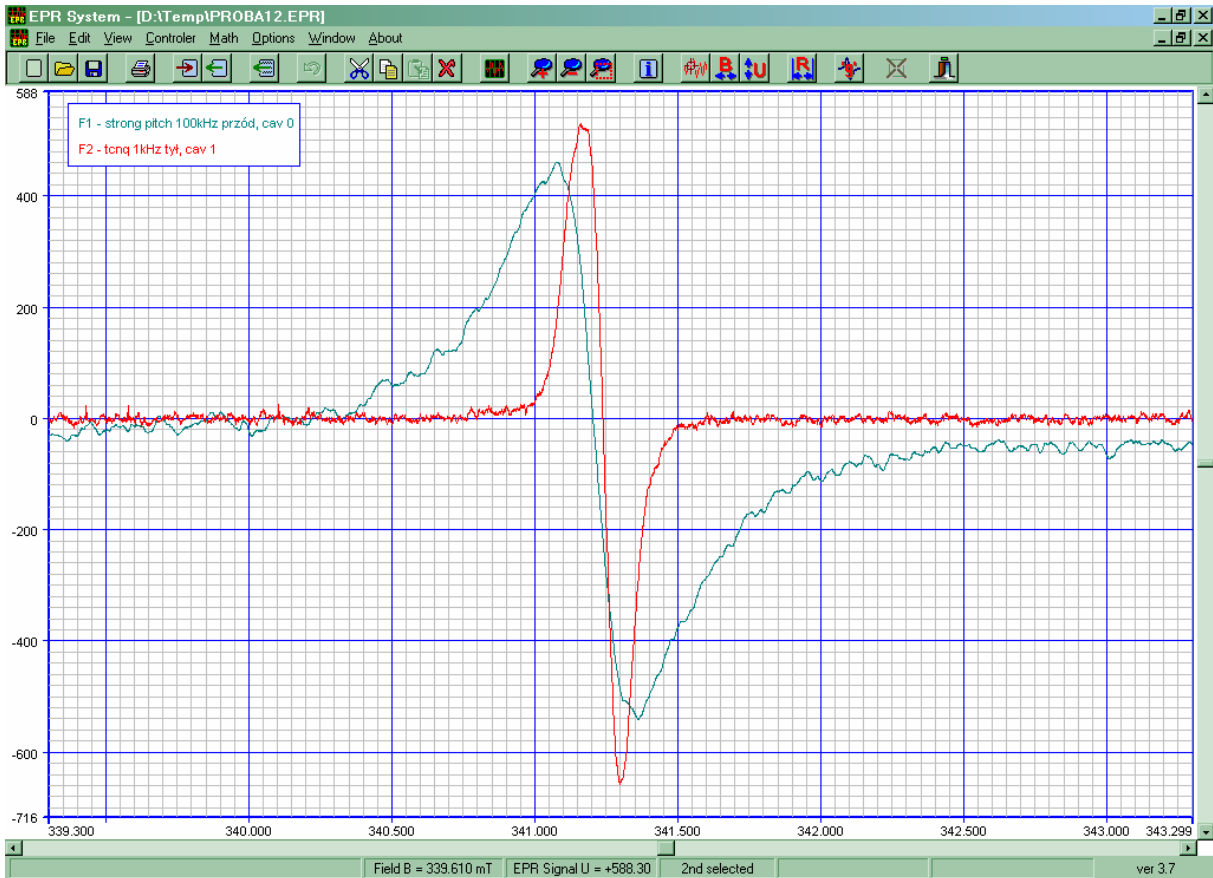


Fig. 6. Edition window view of the control program

The control program has been designed for Windows 2000/XP system. While the spectrometer is controlled via USB interface, every modern computer including notebook can be used. The most important features of the control program are as follows:

1. The full control of the all new, digitally controlled units: digital field controller, digital modulator-receivers 1kHz and 100kHz, microwave frequency meter, NMR magnetic field meter, temperature controller etc.
2. Simultaneous recording of signals coming from two samples
3. Advanced mathematical processing of recorded spectra: smoothing and filtering, addition and subtraction, integrating, differentiation, multiplying through the constant and through the function, comparison and approximation, accounting of special parameters (line width, g factor, intensity).
4. multiple recording with simultaneous accumulation and averaging.

5. Summary

The above described 2-channel EPR spectrometer is especially assigned for quantitative intensity measurement in respect to reference sample. Such a spectrometer is not offered by any commercial company. Bruker Co. offers the double rectangular resonator ER 4105DR as additional equipment for typical EPR spectrometer fitted with only one signal channel. It makes possible quantitative measurements in respect to reference samples only if both signals (of tested sample and of reference sample) are of similar level, however. In other cases a weak signal will be suppressed by a strong signal. In the 2-channel spectrometer with two independent modulator-receivers there is a great possibility of optimal settings. Since the both units are fitted with modulation amplitude control in the range of 80dB, gain control in the range of 80dB and time constant controlled in the range of 1-10000 [7, 9], the ratio between both, good yet recorded signals can be higher than 100dB. In spectrometer with only one signal receiver this is really impossible.

It is to take in an account that the 2-channel EPR spectrometer, giving a new experiment possibilities can be easily built by an advanced upgrade of an older EPR spectrometer. The new needed units are: digital field controller, digital receivers 1kHz and 100kHz, double resonator and modern computer with special control program. The rest of the old spectrometer as microwave unit, electromagnet, electromagnet power supply, console, frequency and field meter (if they exist) are used.

Literature

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