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Electron Paramagnetic Resonance (EPR) Spectrometer for the measurement of the number of spins in investigated materials

1. Introduction

EPR Spectrometry belongs to analytical methods suitable for the examination of important features of the matter. One can distinguish two basic pathways of measurements with the use of this method:

- a. Recording of the EPR signals in order to identify in the examined material homogenous or composed of several component, of paramagnetic species which are characterized by the presence of unpaired electrons (spins) in the molecule, such as paramagnetic centers in crystals, free radicals in organic and biological systems, paramagnetic ions of metals incorporated with complex compounds. Each of these species give rise to a specific signal in EPR. Spectral analysis of the shape of the recorded spectra especially those revealing the hyperfine splitting enables us very often to assign the EPR spectrum to a definite radical, paramagnetic centre etc. It is also possible from the EPR records to draw conclusions as to spherical structure of identified radicals or the localization of specified paramagnetic centre in crystal lattice.
- b. Registration of the EPR signal identified or not, in order to determine the number of spins in the investigated sample under stationary or dynamic condition as a function of time and temperature or in the course of chemical processes. Quantitative EPR measurements are essential in the determination of the rate of radical processes including their transformations as well as by the evaluation of the stability of paramagnetic species in different media. Quantitative EPR measurements are the basis of radiation dosimetry and are indispensable by the determination of the yields of radiation and photo-chemical processes in which free radicals are involved.

Thus, the more precise EPR quantitative determination of the number of spins are needed in many different fields of science and technology, making possible not only to prove the fact of the presence of paramagnetic species in the inspected sample, but also to control the concentration of paramagnetic species during industrial processes i.e. to control their percentage content in there. It is very often that by the EPR examination of a product the determination of the number of spins followed by the calculation of the contribution of paramagnetic components to the overall mass of the product makes possible to evaluate the rate of the participation of radicals in the proceeding process. The need of such quantitative EPR measurements appears e.g. by conducting the works related to the environmental protection (the majority of processes involved occurs with the participation of free radicals.), by controlling food quality (stable radicals and paramagnetic centers appear in certain food products after their treatment with ionizing radiation. Such treatment is applied as a method of preservation and pasteurization of food), in chemical industry (control of paramagnetic intermediates), in petroleum industry (crude oil is often polluted with paramagnetic vanadium compounds and coal particles detectable by EPR method). Quantitative measurements are essential in radiation EPR dosimetry enabling the determination of dose of ionizing radiation with the use of calibrated dose meters e.g. powdered L-alanine attached in the form of pellets to medical products undergoing radiation sterilization as well as to foodstuffs pasteurized by irradiation. The problem is essential since in view of presently obeying regulations (Codex Alimentarius and EU Directives) radiation treated food must be labeled while in European Union only three groups of food are allowed to be irradiated: spices, herbs and seasonings. It means that irradiation and distribution of the other food products is in Europe prohibited.

In principle the quantitative measurement could be done with any EPR spectrometer. However, in practice it is very difficult and often quite impossible task to be simply done, since quantitative method requires applying of appropriate reference standard samples which should be measured simultaneously with the sample. Moreover, the relation between the number of spins registered by EPR signal and the number of spins in the sample depends from many factors often difficultly determined. Below three important factors influencing quantitative EPR measurements of the number of spins are listed, while two first of them are very difficult for estimation.

1. The value of the magnetic component of the microwave electromagnetic field inside of the inspected samples. This value depends on the property of the sample, on the level of the microwave power inside the sample, on the structure of the sample and on the Q-factor of the measuring resonator;
2. Coupling rate of the inspected sample with the measuring resonator. It depends, among the others on the relationship between the volume of tested sample and the volume of the measuring resonator;
3. Effective amplifying factor of the receiver path and the level of the field modulation. These parameters are relatively easier to be determined.

In what a way the quantitative EPR measurements can be accomplished in practice?

Since the direct determination of the number of spins is very difficult, a comparative method for quantitative EPR measurements are most often applied, in which the registered EPR signal of the tested sample is compared with the registered EPR signal of standard sample with the known number of spins estimated. The comparative method can be executed by different ways:

1. Under possibly identical condition two independent registrations of EPR signals are being done one by one i.e. with standard sample and with tested sample, respectively. It is the simplest way of quantitative EPR measurement, but not very certain in practice since usually it is very difficult to assure the same conditions in the course of both measurements, especially when the differences between physical and electron density as well as between the numbers of spins in the standard and tested samples are considerable large.
2. Simultaneous recording of the EPR signal of tested sample and of standard sample, both placed inside the same tested measuring ampoule. This method is much more reliable as compared with the previous one – both signals are being recorded under the same conditions. However, in practice it is very difficult to insert a standard sample inside the inspected sample while very often the overlapping of the EPR signals from both sample and standard is observed making impossible the proper estimation of the intensity or amplitude of both.
3. Application of double resonator, containing two identical measuring chambers with possibly similar distribution of the microwave electromagnetic field in both. In one chamber the tested sample is inserted while the reference sample is placed in the second chamber. Such configuration guarantees that both samples are measured nearly under the same condition. Double resonator is being constructed typically by appropriate folding of two identical rectangular resonators TE₁₀₂ mode resulting in one double rectangular resonator with TE₁₀₄ mode. The Bruker Company offers such X-Band double resonator (model ER 4105DR) with the information that it is particularly suitable for quantitative measurements. The application of the double resonator ensures greater accuracy in determination of the number of spins as compared with two above described ways but under condition that both signals of tested sample and reference sample contain similar numbers of spins. It is so since both EPR signals are being recorded simultaneously with the same receiving path, so in order to avoid masking the weak signal by the stronger one, both signals must be characterized by similar intensity. It is necessary to assure, therefore, that the numbers of spins in both samples will be comparable. However, the fulfillment of the above condition is in most cases impossible and it is necessary to apply many of reference samples or of the set of reference samples representing different numbers of spins. Consequently, the accuracy of the measurement is markedly decreased remaining not better like in the case of applying the external standard sample (pt. 1).

4. Application of the double resonator (similarly as in the above described method) but two independent receiving paths of the EPR signal: one for the signal from the tested sample and second for the signal from the reference sample. In order to avoid the mutual interference in the system, the frequencies of both paths should much differ between themselves; the optimum choice is **100 kHz** for the tested sample path and **1 kHz** for the reference sample path. Since basic parameters (modulation amplitude, effective amplifying factor, width of the frequency band) of both receiving paths can be selected independently, so the intensities (amplitudes) of the EPR signals from both samples can differ themselves even by a few orders. With the resonator of such configuration only one reference sample can be applied for the measurements with many samples differing much in the numbers of spins. In this case, however, a special computer system is needed enabling simultaneous recording of signals from both paths.

2. Two-channel EPR spectrometer

The idea of two-channel spectrometer is known and described in textbooks compiling technical aspects of EPR spectrometry [1, 2]. However it is rather only rarely adapted in practice. The main reason is that such system must consist of almost two spectrometers, cooperating simultaneously with one double resonator. As to our knowledge, none of commercial companies offers this kind of spectrometer today. In 1982 the Varian EPR X-Band spectrometer has been reconstructed [3, 4] and equipped with additional LF receiver (from the Q-Band spectrometer) to be transformed in the two-channel spectrometer enabling simultaneous recording of the EPR signal from two samples. The X-Band double resonator was of two rectangular resonators of the TE₁₀₂ mode, joined together with an narrow wall, creating the 2-chamber resonator of the TE₁₀₄ mode. Such solution enables to conduct the quantitative measurements with a very high accuracy not attainable with the use of a classic EPR spectrometer. The simplified block diagram of the two-channel spectrometer is presented in Fig. 1.

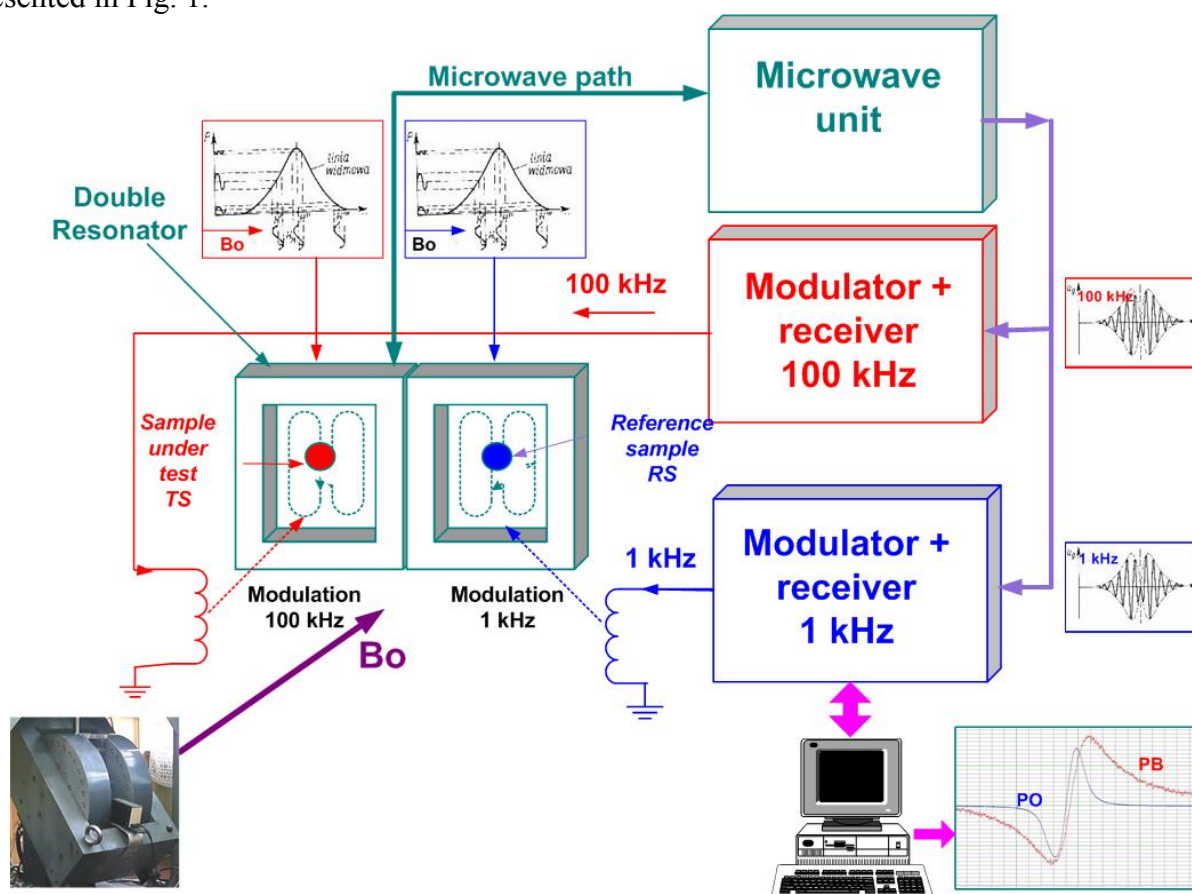


Fig. 1. Block diagram of the two-channel EPR spectrometer

2.1 Double resonator

The essential element of the two-channel EPR spectrometer is the double resonator, which assures possibly similar conditions of the recording of signals from both standard and tested samples.

Below two possible solutions enabling to construct two-channel are given:

- Double resonator consisting of two resonators and forming the 2-chamber resonator
- Two independent and identical resonators connected in such a way that none of them influence the other although their initial signals are summed.

2.1.1. Rectangular 2-chamber resonator

The 2-chamber rectangular resonator is constructed through appropriate folding of two identical, rectangular resonators of TE102 mode; as the result the TE104 mode resonator is created having two identical chambers closely coupled with oneself. The example of such resonator for the X-Band is shown in Fig. 2. Since the sizes of the rectangular resonator is inversely proportional to the frequency band, so the described solution can be applied only for the X- and Q-Band spectrometers. The illustrative schema of the X-Band two-channel spectrometer is shown in Fig. 3. In this spectrometer the two-chamber resonator as shown in Fig. 2 has been adapted.

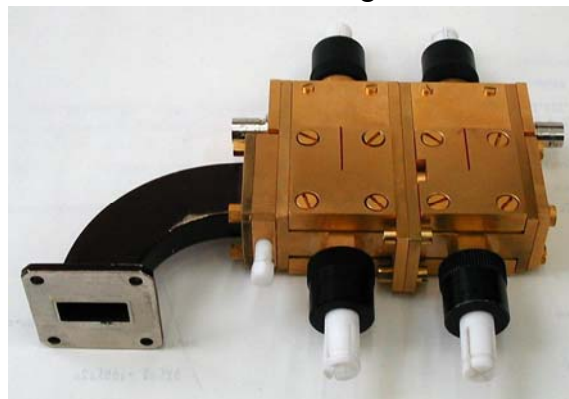


Fig. 2. X-Band double resonator with mode TE104

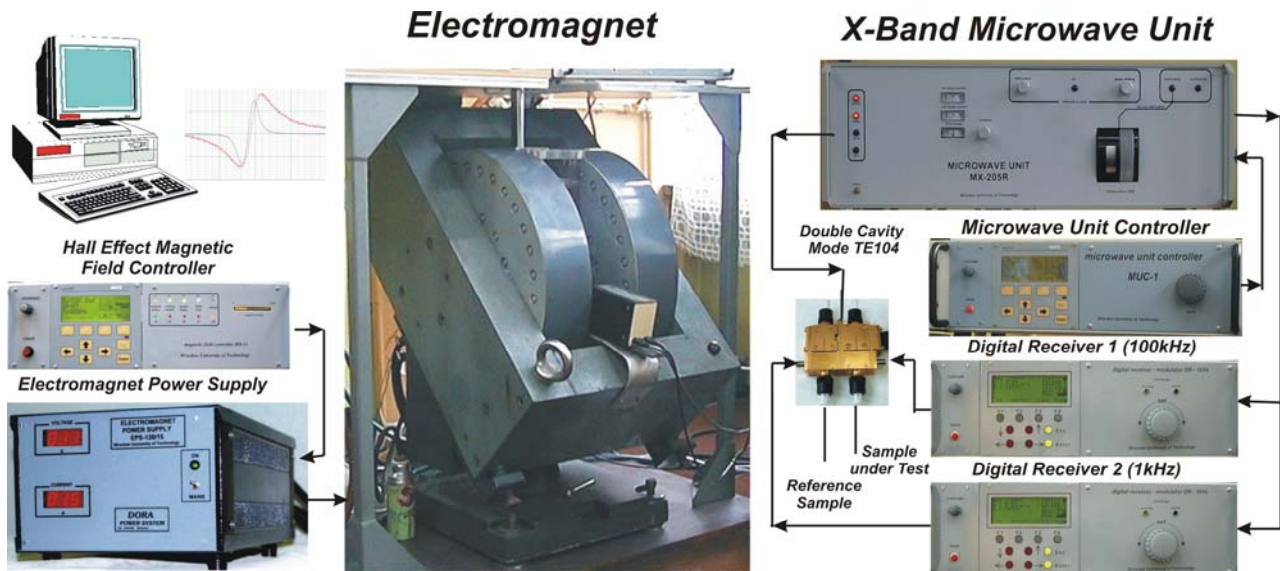


Fig. 3. Illustrative schema of the two-channel X-Band EPR spectrometer with the TE104 mode double resonator

2.1. 2-chamber resonator of the type Loop-Gap

The construction of typical Loop-Gap resonator having two chambers coupled one with the other with a gap between is shown in Fig. 4 [5].

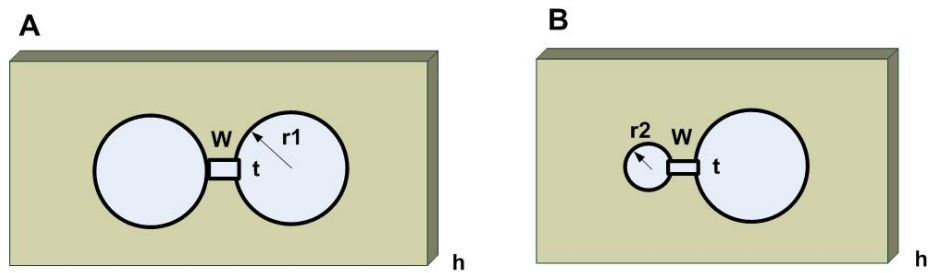


Fig. 4. Loop-Gap resonator with two cylindrical cavity coupled with a gap. A- construction used for lower frequency bands (UHF, L, S), B – construction used for higher frequency bands (X, Q). where h , r – length and radius of the cavity respectively, W , t – width and length of the gap respectively

Under the development project No. N R01 018 04 supported by NCBiR and entitled „**The prototype of the EPR spectrometer for dosimetric measurements and for the identification of irradiated food**” the complete L-Band EPR spectrometer has been designed and constructed in which the Loop-Gap resonator shown in Fig. 5 was adapted [6 - 10].

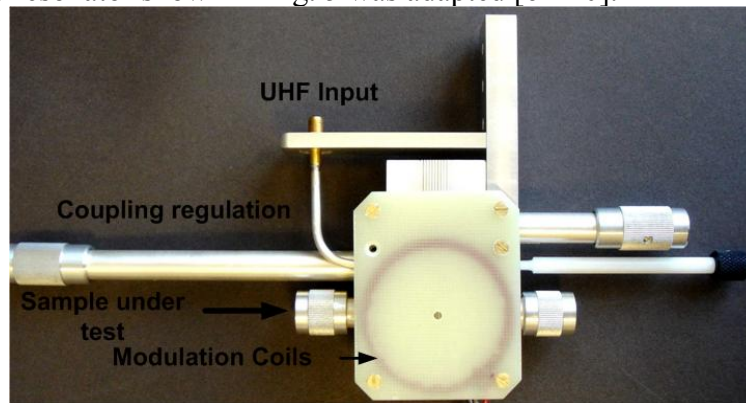


Fig. 5. Loop-Gap resonator used in the designed L-Band EPR spectrometer

In Fig. 6 the L-Band Loop-Gap resonator is shown especially designed to be applied for the L-Band two-channel EPR spectrometer.

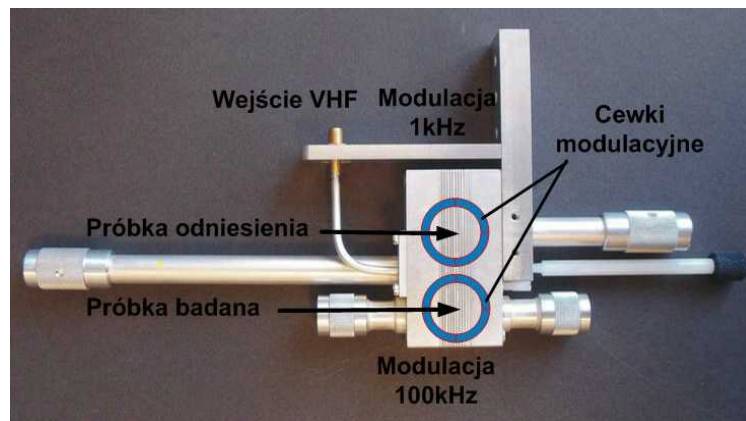


Fig. 6. Loop-Gap resonator for two-channel L-Band EPR spectrometer

Due to the relatively small distance between both measuring chambers, the diameter of modulation coils should be small enough to generate magnetic fields that will not influence mutually both chambers.

2.1.3. Two independent resonators

It is possible to create the double resonator from two identical resonators incorporated with the system so that each of them will not be influenced by the other although the signals originating from them will be added. The model scheme of connecting two resonators in the microwave unit is shown in Fig. 7.

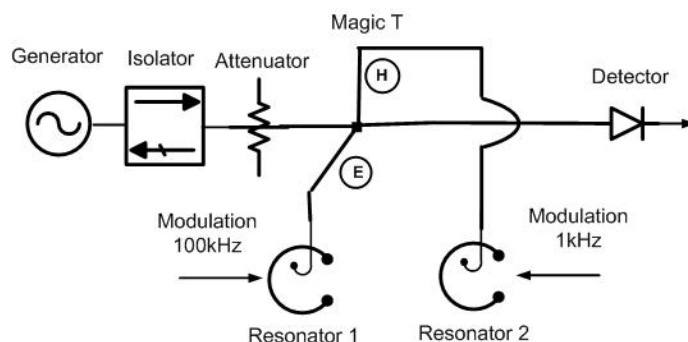


Fig. 7. Manner of the proper connection of two resonators in microwave unit

3. Control program

The computer control program **EPR System** has been designed especially to control of the units of designed spectrometer (magnetic field controller, EPR signal digital receivers of the 1kHz and 100kHz frequency and microwave unit) via the USB interface, guaranteeing the simultaneous recording of both EPR signals. Additionally, the program enables an advanced digital processing of registered signals (smoothing, adding, integrating, mutual comparing, differentiating etc.). The program can also cooperate with other, additional measuring instruments (controlled via USB or RS232 interface) as NMR magnetic field meter, frequency and microwave power meter and temperature controller of the tested sample and other. The main window of the program EPR System is shown in Fig. 8. Owing to applied USB interface, the program EPR System can be installed both in the stationary computer (desktop) as well as in notebook.

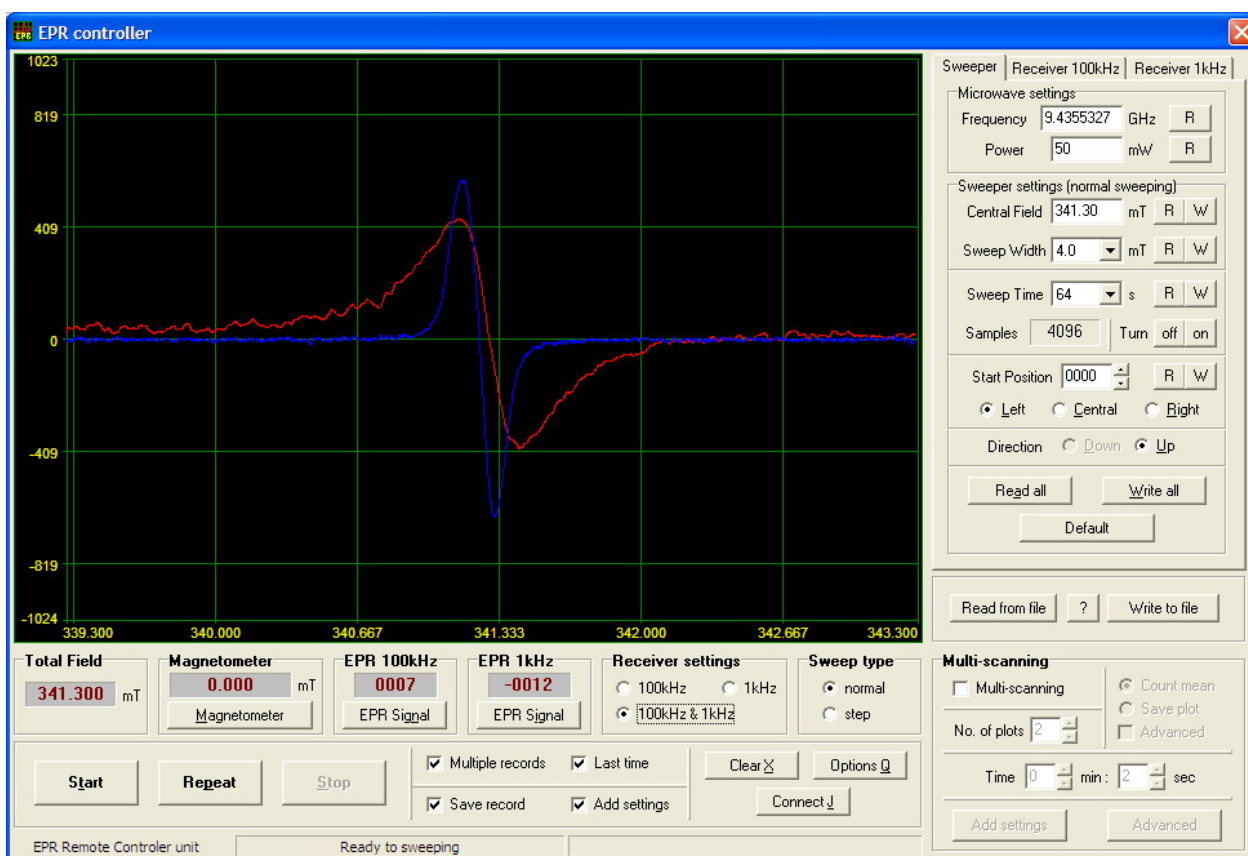


Fig. 8. Main window of the program EPR System

4. Examples of the realizations

As earlier already mentioned, no commercial company offers two-channel EPR spectrometer, being suitable for relative measurements of the intensity of EPR signals. Such spectrometer may be built under the upgrading of an older EPR spectrometer. During the last years the team of the

Wroclaw University of Technology has built three two-channel X-Band EPR spectrometers shown below in Figures 9 and 10.

a. Medical Academy in Bydgoszcz and the University in Białystok

Two-channel X-Band EPR spectrometers built on the basis of EPR spectrometers produced by Radiopan Company in Poznań non-existing today.



Fig. 9. X-Band two-channel EPR spectrometers in the Medical Academy in Bydgoszcz and in the University in Białystok

b. The Institute of Physics of the Polish Academy of Sciences in Warsaw

The X-Band two-channel EPR spectrometer built on the basis of the EPR spectrometer produced earlier (1975) by the Wroclaw University of Technology

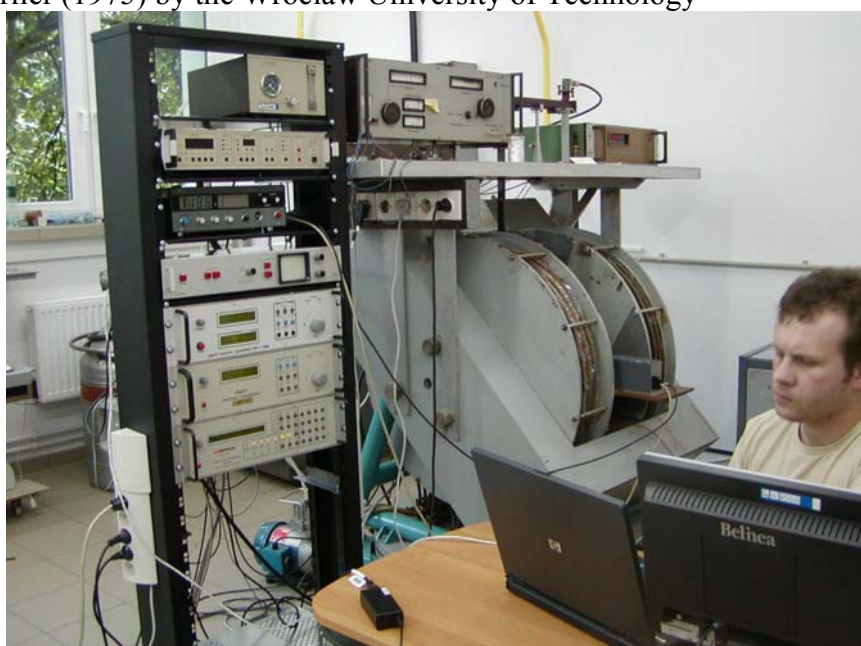


Fig. 10. X-Band two-channel EPR spectrometer in the Institute of Physics of the Polish Academy of Science in Warszawa

5. Summary

The above considerations supported by presented solutions show conclusively that at relatively low financial outlay it is possible to receive a new tool for advanced research in the field of EPR spectroscopy, not offered so far by the world EPR instruments industry. The possibility of conducting the accurate measurements of the intensities of EPR signals is very important almost in all fields of science and technology in which the EPR spectrometry is used.

For the construction of such kind of spectrometers especially suitable is the L-Band spectrometer designed by our team. By adding to this spectrometer the digital EPR signal receiver of the

frequency of 1 kHz and slightly changing the construction of the applied resonator Loop-Gap, a two-channel L-Band EPR spectrometer of a new generation can be created.

Such kind of spectrometer is especially suitable for the measurements of doses of ionizing radiation in irradiation facilities by sterilization and pasteurization of different materials including food. Since suppression of electromagnetic field by water in L-Band is much lower than in higher frequency microwave bands (X, K, Q), the L-Band spectrometer is exceptionally useful in testing of substances with a large content of water. The content of water is a typical feature of the majority of food and biological materials. In contrast to L-Band, the samples with a big content of water are with difficulty or non measurable at higher frequency bands (X, K, Q).

It is possible to anticipate that such kind of spectrometer would find application in both research and industrial units as well as in control laboratories of different profile, which are involved in the examination, processing and distribution of radiation treated biological materials including food of domestic and foreign origin.

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Electron Paramagnetic Resonance (EPR) spectrometer for quantitative measurements of the spins number in the sample under test

Summary

The construction of the two-channel EPR spectrometer, enabling quantitative measurements of the spins number with regard to the model sample has been described. A such spectrometer consists apart of standard blocks (microwave unit, receiver of EPR signal and magnetic field stabilizer) and of the double measuring resonator, the additional EPR signal receiver and the control program enabling simultaneous recording of the EPR signal of the sample under test and of the reference sample. A rebuilding of the designed L-Band EPR spectrometer to be suitable for quantitative dosimetry of the irradiated food has been considered.