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L-BAND ESR SPECTROMETER USING A LOOP-GAP RESONATOR FOR *IN VIVO* ANALYSIS

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An L-band ESR spectrometer using a loop-gap resonator with an electric shield was constructed in order to measure large quantities of wet biological samples at *in vivo* state. The principal components of the loop-gap resonator and the comparison of the sensitivity between X-band cavity and the loop-gap resonator were described.

Electron spin resonance (ESR) techniques have been used to study the processes involving free radical in various systems. Generally, it is difficult to obtain the ESR spectra of large quantities of wet biological samples with an X-band resonant cavity because of a high dielectric loss of water. Therefore, various attempts have been made for such measurements. For example, a surface coil,[1] a loop-gap resonator,[2,3] and a re-entrant resonator[4] are very hopeful.

In this study, an L-band ESR spectrometer using a loop-gap resonator with an electric shield behind a gap was constructed as a trial in order to analyze the large quantities of the biological systems at the *in vivo* state.

The outline of our L-band ESR system is as follows. The incident microwave frequency is about 1 GHz of L-band. In this region, a dielectric absorption of water is very small in comparison with X-band.[5] The resonant magnetic field of free radical is about 300 gauss (= 10^{-4} T) as estimated from the resonance equation, and therefore it is possible to widen the space between the two magnetic poles of the electromagnet. The distance between the two poles is 120 mm in our electromagnet. For the purpose of *in vivo* analysis, the selection of a resonator is most important. In our study, the loop-gap resonator was used.

The loop-gap resonator has been applied first to ESR by Froncisz and Hyde as a very high sensitive resonator.[2)] The size dimensions of the loop-gap resonator for an L-band ESR was calculated from the semi-empirical equation in the literature.[2,6)] In addition, an electric shield was newly performed behind the gap in this work. The electric shield is composed of teflon spacer and aluminum foil sheet. This shield is our original idea, and is effective to the suppression of the fringing electric field in the loop. Figure 1 shows the principal components of our loop-gap resonator, and their dimensions are given in Table 1.

The microwave circuit was constructed with a synthesized oscillator, a circulator, a stub tuner, a low noise amplifier, a frequency mixer, a phase shifter for a homodyne detection, and so on, which were connected with a frexible coaxial cable. The magnetic field modulation of 100 kHz was employed with a pair of coils

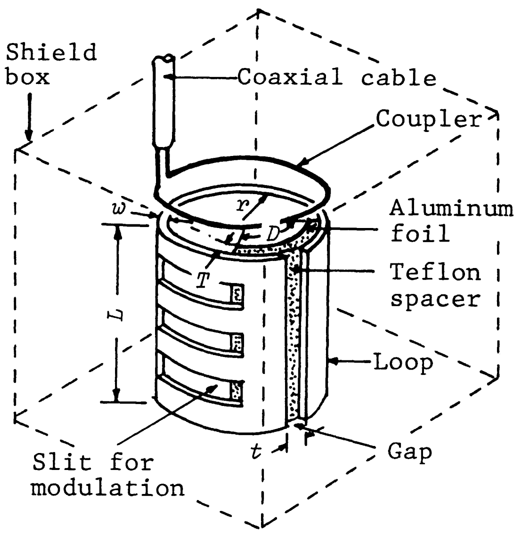

Fig. 1. The principal components of the loop-gap resonator with electric shield. A sample is inserted into the loop through the holes at the top or the bottom of the shield box.

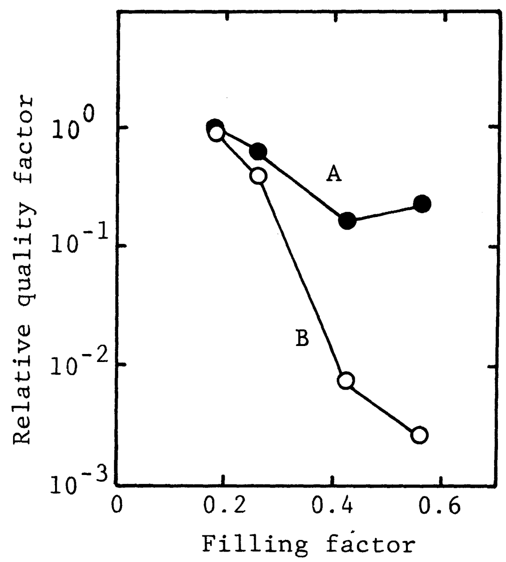

Fig. 2. Variation of quality factors of the resonator with (A) and without (B) an electric shield. Filling factor was ajusted with a physiological salt solution.

Table 1. The dimensions of the loop-gap resonator with an electric shield (mm)

r	*t*	*w*	*L*	*D*	*T*
14.5	5.0	0.5	28.5	22.8	2.2

in the shield box. The electromagnet and the other instrument were of JEOL FE-3X X-band ESR spectrometer.

Figure 2 shows the variation of the quality factor of two loop-gap resonators with and without the electric shield in the loop. Each value of quality factor was obtained by using a physiological salt solution. Filling factor is the ratio of the volume of salt solution to the inner volume of the resonator. As shown in the figure, the decrease of the quality factor of resonator A was smaller than resonator B when the quantities of the salt solution became larger. This means that the sensitivity of the resonator A with the electric shield is higher than the resonator B, and that the fringing electric field was extremely restrained by the electric shield in the loop.

Figure 3 shows the comparison of the sensitivity between the X-band cavity and our loop-gap resonator. The X-band cavity used is of a JEOL TE_{011} type. The ESR spectra of an aqueous solution of 2 x 10^{-5} M (= mol dm^{-3}) 4-hydroxy-2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPOL) radical were measured at the same conditions. Figure 3(a) is the X-band ESR spectrum of radical solution in a usual flat cell of 0.1 ml volume, and Fig. 3(b) is the L-band ESR spectrum of 10 ml sample solution obtained by our L-band ESR system. Three line signals are the typical hyperfine structure due to a nitrogen atom in TEMPOL molecule. The signal-to-noise ratio of L-band ESR signal was 10 times lower than that of X-band one. However, it is noteworthy that the signal height of L-band signal was almostly equal to that of X-band one. The high noise level of L-band was found to be due to the carrier noise of the oscillator. Therefore, it will be important in the future that the carrier noise is removed as much as possible in order to obtain the spectra with the higher signal-to-noise ratio.

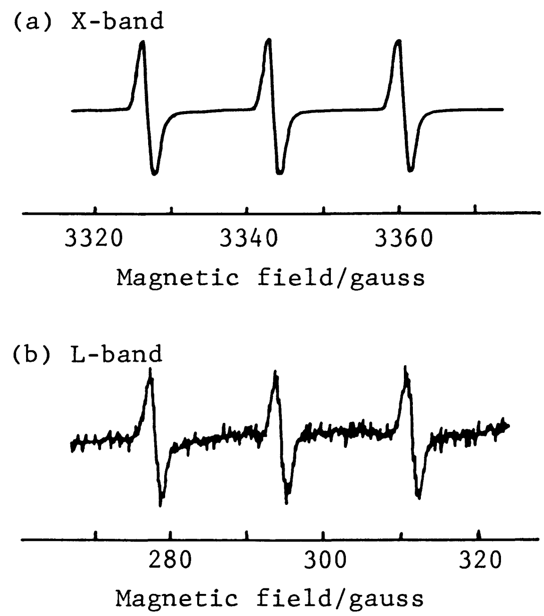

Fig. 3. Sensitivity comparison examining an aqueous solution of 2 x 10^{-5} M TEMPOL in a JEOL TE_{011} X-band cavity and our L-band loop-gap resonator, where amplitude is 2.5 X 100, microwave power 8 mW, modulation 1 gauss, and response time 0.01 s. Sample volume for X- and L-band measurements is 0.1 and 10 ml, respectively.

Figure 4 shows the L-band ESR spectrum of a test sample holding a small glass ball in water. The glass ball involves 0.3 ml of 1 x 10^{-3} M TEMPOL aqueous solution. Even though the ball was placed at the top or at the bottom of the test tube, and the radical in the ball was dispersed into bulk water, the same signal intensity was observed.

These results indicate that our loop-gap resonator operated as was expected, and that the loop-gap resonator with the electric shield will be used as a powerful tool for the *in vivo* analysis of large quantities of wet biological systems. Furthermore, this loop-gap resonator will be also applied to the non-destructive measurements of large volume samples other than biological systems. Various applications of our L-band ESR spectrometer are now being investigated in our laboratory.

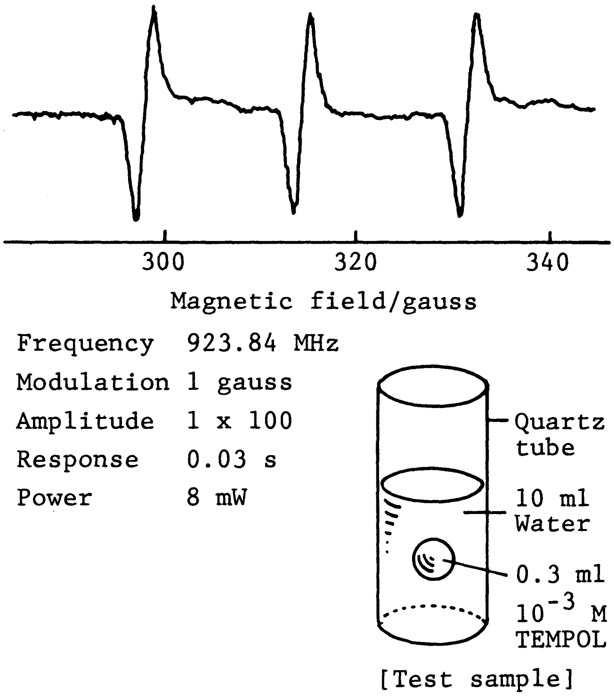

Fig. 4. L-band ESR spectrum of test sample obtained at room temperature.

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