Recent progress in nuclear magnetic resonance (NMR) spectroscopy has made it possible to observe several significant nuclei which frequently appear in organic compounds using a single broad band probe. Despite the importance of $^{35}$Cl-NMR observation in order to investigate various inorganic Cl salts, perchlorate, and some kind of gels, $^{35}$Cl has not been covered in conventional broad band probe ($^{31}$P–$^{15}$N). Generally, we have been measured such a low resonance frequency as that observed in $^{35}$Cl nucleus, having a lower magnetogyric ratio ($\gamma$) than those in $^{15}$N, by using a customized probe. Here we developed a new broad band probe covering $^{35}$Cl-NMR frequencies. This probe is easily converted from commercially available conventional probe at a low cost and makes it possible to observe $^{35}$Cl-NMR by a sample tube ordinarily used for $^1$H- and $^{13}$C-NMR experiments.

An additional stick (stick-shaped resonance frequency switcher) was designed to extend the observed resonance frequency. Figure 1 exhibits a schematic circuit diagram of the probe, which performs the high frequency coverage for $^{19}$F and $^1$H of 470.55–500.13 MHz, and NMR lock frequency of 76.77 MHz (D). The newly developed stick-E for $^{35}$Cl-tuning was additionally equipped with the low frequency (LF) module. Further tuning was done by adjusting a couple of variable capacitors, LF-match and LF-tune (Fig. 1). The range from $^{31}$P to $^{35}$Cl nucleus (202.47–49.0 MHz) is covered by using this probe with the stick. The figure of the stick E working as a capacitor in $^{35}$Cl-NMR observation is shown in Fig. 2. An inductor that will be able to eliminate the unfavorable coherent signals interfering with the low frequency circuit caused by the extension of the lower band was connected in series to the tip-condenser having a

Fig. 1 Circuit diagram of the new broad band probe.

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capacitance of 39 pf. The estimated circuit $Q$ factor was around 50 for $^{35}$Cl-NMR frequency. No disadvantage in detecting other nuclei was observed by the addition of this stick.

This new broad band probe system using 5 mm o.d. sample tube was adopted to analyze several compounds containing chlorine atoms. The 90° pulse width for 1.2 mol/L NaCl aqueous solution was measured to be 30 $\mu$s. It was found to be useful for observing Cl ionic species such as NaCl in aqueous solution, whereas relatively low detection sensitivity and broadening of the $^{35}$Cl signal was observed in the case of neutral chlorine atom. An analysis of the alkaloid (quaternary salt) by using this probe is presented. $^{35}$Cl-NMR measurements of berberine·HCl (5 mg/0.5 mL D$_2$O) and tetrahydroberberine·HCl (10 mg/0.5 mL CD$_3$OD) with 1000 – 3000 scans (relaxation delay = 0.1 s) were successful. The spectra for these compounds were shown in Fig. 3. The sensitivity of $^{35}$Cl on this probe was comparable to that of the conventional lower band probe covering this nucleus.

It was proved that the facile measurement over a wide range of observable elements by an identical probe as presented here is quite possible, including chlorine atoms which have low resonance frequencies in NMR spectroscopy.

Fig. 2 $^{35}$Cl-NMR tuning stick. The rod is shown as an arbitrary length.

Fig. 3 $^{35}$Cl-NMR spectra of tetrahydroberberine·HCl (a) and berberine·HCl (b). 1.2 mol/L NaCl aqueous solution was referenced to 0 ppm as an external standard.

References