Measurement of Cole-Cole Plot for Quality Evaluation of Red Wine

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Abstract. *For the aim of evaluating the quality of red wine, we measured the complex relative permittivity in the frequency range from 100 MHz to 40 GHz with a network analyzer, and showed that the Cole-Cole plot of red wine consists of a semicircle at frequencies above around 1 GHz and straight line at frequencies below 1 GHz, which come from the dispersion properties for the water solution of alcohol and ingredients peculiar to red wine, respectively. Based on the measured Cole-Cole plots for seven kinds of red wines made from the same brand of Merlot in different production years, Debye dispersion parameters were estimated to reveal that the alcohol concentration and ingredient property can simultaneously be estimated from the parameters for the semicircle and straight line, respectively.*

Keywords: Red wine, Cole-Cole plot, dispersion parameters, alcohol concentration, ingredients.

1. Introduction

Quality that guarantees the taste of alcoholic drinks is being evaluated by measurement of alcohol concentration, chemical analyses of ingredients and expert's sensuality test, which require a great deal of time and labour.

For the aim of evaluating the quality of red wine, we previously measured the complex relative permittivity in the frequency range from 10 MHz to 6 GHz with a network analyzer, and estimated the Cole-Cole plot parameters of red wine, which exhibited that the alcohol concentration of red wine can be estimated from the parameters for semicircle dispersion in the Cole-Cole plot, and other ingredients can also be evaluated by the parameters for straight line dispersion [1, 2].

The developed method allows to simply estimating the concentration of alcohol in drinks containing various flavour substances (ingredients) like in the wine. No fractional distillation is necessary for test. We assumed that the shape of semicircle and straight line on Cole-Cole plot should characterize the dispersion properties of the water solution of alcohol and ingredients peculiar to red wine, respectively

In the present study, to validate this assumption, we measure the complex relative permittivity of red wine, its distillation and residue after distillation in the frequency range from 100 MHz to 40 GHz, and compare their Cole-Cole plots to show how the alcohol component and other ingredients should affect the dispersion properties of the Cole-Cole plot. Based on the measured Cole-Cole plots, Debye dispersion parameters are also estimated to show their dependence on elapsed production years of seven kinds of red wines made from the same brand of Merlot.

2. Method

Figure 1 shows a setup for measuring complex permittivity with a dielectric probe. Liquid samples used for estimating alcohol concentration were pure water and dilute ethanol solution, whose complex relative permittivity was measured in the frequency range from 100MHz to 40GHz with the dielectric probe connected to a network analyzer.

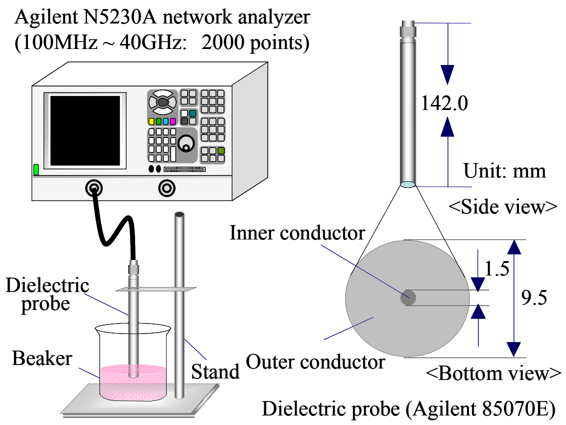

Fig. 1. Setup and configuration of dielectric probe for measurement of complex permittivity.

The complex relative permittivity of red wine including conductive impurities [3] can be expressed as

$$\left.\begin{aligned}
\varepsilon_r^* &= \varepsilon_r' - j\varepsilon_r'' = \varepsilon_{r\infty} + \frac{\varepsilon_{r0} - \varepsilon_{r\infty}}{1 + (j\omega\tau_0)^\beta} + \frac{1}{(j\omega\tau)^\alpha} \\
\varepsilon_r' &= \varepsilon_{r\infty} + \left\{1 - \frac{\sinh(\beta \ln \omega\tau_0)}{\cosh(\beta \ln \omega\tau_0) + \cos\frac{\beta\pi}{2}}\right\} \times \frac{\varepsilon_{r0} - \varepsilon_{r\infty}}{2} + \left\{\cosh(\alpha \ln \omega\tau) - \sinh(\alpha \ln \omega\tau)\right\} \times \cos\frac{\alpha\pi}{2} \\
\varepsilon_r'' &= \frac{\sin\frac{\beta\pi}{2}}{\cosh(\beta \ln \omega\tau_0) + \cos\frac{\beta\pi}{2}} \times \frac{\varepsilon_{r0} - \varepsilon_{r\infty}}{2} + \left\{\cosh(\alpha \ln \omega\tau) - \sinh(\alpha \ln \omega\tau)\right\} \times \sin\frac{\alpha\pi}{2}
\end{aligned}\right\} \quad (1)$$

where ε_{r0} is the DC relative permittivity, $\varepsilon_{r\infty}$ is the relative permittivity at infinite frequency, α and β represent the degree of relaxation distribution, τ and τ_0 are the relaxation time constants. For pure water or dilute ethanol solution without DC conductivities, the first and second terms on the right hand side of Eq. (1) are used.

Eq. (1) shows that Cole-Cole plot or ε_r' - ε_r'' curve consists of a semicircle and straight line, which can be represented by the first and second terms and the third term, respectively, on the right hand side of Eq. (1).

According to Ref. [2], the alcohol concentration of red wine is assumed to be evaluated from the parameters of ε_{r0}, $\varepsilon_{r\infty}$, τ_0 and β in Eq. (1), which was estimated in the following way. Measurement of the Cole-Cole plots was made for pure water and dilute ethanol solution, which were fitted to Eq. (1) without the third term to reveal the dependence on alcohol concentration of the above-mentioned parameters for calibration data. The parameters in Eq. (1) were also obtained from the Cole-Cole plot measured for red wine, whose alcohol concentration was estimated from the calibration data for pure water and dilute ethanol solution, and was validated by using a distillation method [2].

In order to verify the validity of the above-mentioned assumption, we compared the Cole-Cole plots measured for pure water, red wine, its distillation and residue after distillation in order to examine how alcohol component can affect these Cole-Cole plots. For red wines to be measured, we used seven kinds of Japanese red wines made from the same brand of Merlot in different production years, which were named here A, B, C, D, E, F and G.

3. Results and discussion

Figure 2 shows the Cole-Cole plots measured and calculated for pure water, wine A, its distillation and residue. Table 1 summarizes Cole-Cole parameters and their estimated values of wine A, distillation and residue. The estimated alcohol concentration of wine A was 12.2 %, which agrees well with the measured alcohol concentration (12.1%) from a distillation method. We found from Fig. 2 that there is good agreement between measurement and calculation by Eq. (1). The results also show that the pure water and distillate have only semicircles in the Cole-Cole plot, while wine A and its residue have both of semicircles and straight lines. It should be noted that the semicircles of wine A and the residue approximately agree with those for the distillation and pure water, respectively. This means that the semicircle and straight line are essentially derived from the dispersion properties of alcohol component and specific ingredients of red wine.

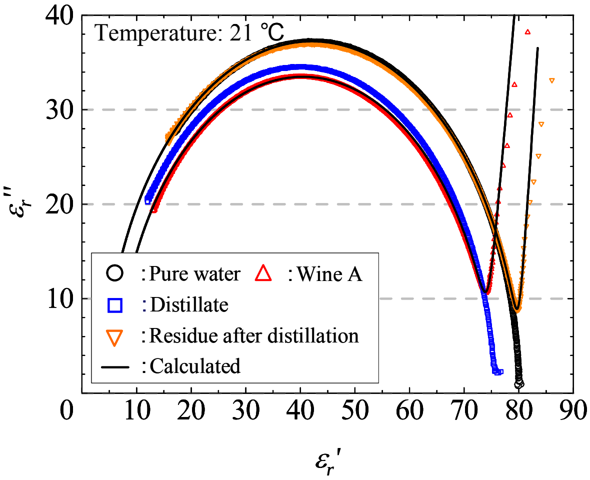

Fig. 2. Measured and calculated Cole-Cole plots.

Figure 3(a) shows the Cole-Cole plots measured for six kinds of wine B to G with the same brand of Merlot in different production years. Also shown in Fig. 3(b) is an enlargement of the Cole-Cole plots around the minimum points. These Cole-Cole parameters are summarized in Table 2 together with the estimated values of alcohol concentration. We found that all the semicircle parts almost coincide, which shows the same alcohol concentration for wine B to G despite different production years. There are some differences between the minimum points and gradients of straight lines for the production years, which suggests a possibility that ingredients peculiar to red wine could be evaluated from the corresponding Cole-Cole parameters: τ, α and f_m.

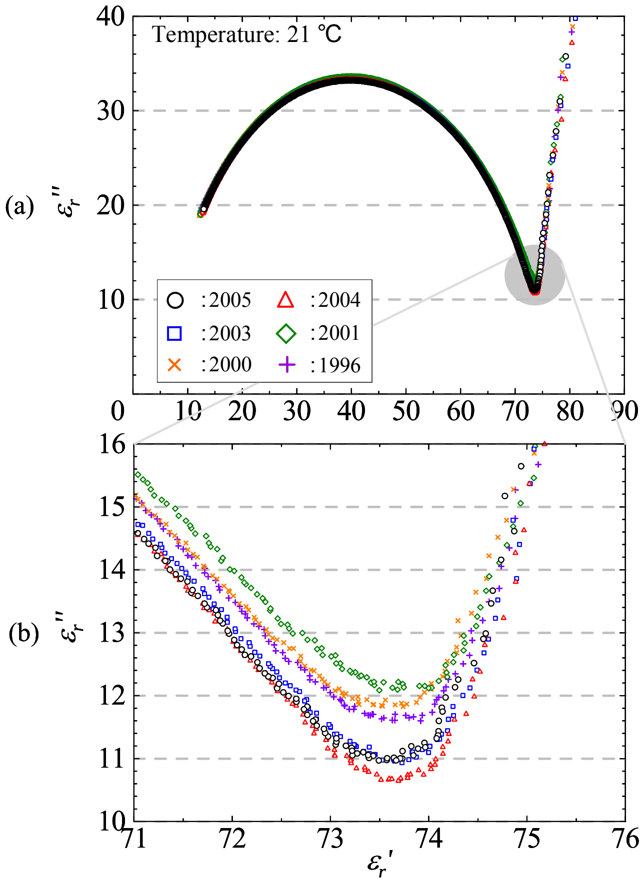

Fig. 3. (a) Measured results of Cole-Cole plots for red wines of different production years and (b) enlargement of the Cole-Cole plots around the minimum points .

Table 1. Cole-Cole parameters and their estimated values of wine A before/after distillation.

Merlot wine	ε_{r0}	$\varepsilon_{r\infty}$	β	τ_0 [ps]	τ [ps]	f_m [MHz]	α
Wine A[2006]	73.6(12.2)	6.2	0.986	12.76	25.70	798	0.910
Distillate	75.5<12.1>	4.9	0.983	12.61			
Residue	79.5	4.0	0.986	9.64	33.50	898	0.930

[ ]: Production year
( ) :Estimated alcohol concentration [%]
< > : Measured alcohol concentration with a distiller [%]
f_m: frequency at which Cole-Cole plot reaches the minimum point

Table 2. Estimated values of alcohol concentration and parameters for Cole-Cole plot of red wines.

Merlot wine	ε_{r0}	$\varepsilon_{r\infty}$	β	τ_0 [ps]	τ [ps]	f_m [MHz]	α
Wine B[2005]	73.4(12.4)	5.6	0.976	12.65	25.30	938	0.916
Wine C[2004]	73.5(12.5)	5.7	0.978	12.94	26.90	858	0.912
Wine D[2003]	73.5(12.5)	5.6	0.976	12.96	25.30	839	0.910
Wine E[2001]	73.5(12.5)	5.5	0.978	13.21	21.00	998	0.911
Wine F[2000]	73.4(12.6)	5.5	0.978	13.24	22.50	918	0.912
Wine G[1996]	73.4(12.6)	5.6	0.979	12.83	21.50	798	0.908

[ ]: Production year
( ) :Estimated alcohol concentration [%]

4. Conclusions

In comparison of the Cole-Cole plots of red wine, its distillation and residue, we confirmed that the semicircle and straight line in the Cole-Cole plot are essentially based on the dispersion properties of the water solution of alcohol and the ingredients peculiar to the red wine, respectively. The dependence on elapsed production years of the Cole-Cole parameters implies a possibility that the maturity of red wine may be evaluated from the dispersion properties of wine characterized by the straight line in Cole-Cole plot.

The future subject is to evaluate the quality of red wine from the Cole-Cole plot in the low frequency region based on TDR (Time Domain Reflectometer) measurement.

References

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