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Cole-Cole Measurement of Dispersion Properties for Quality Evaluation of Red Wine

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In order to evaluate the quality of red wine, measurement of the complex relative permittivity was conducted in the frequency range from 100 MHz to 40 GHz with a network analyzer. Results showed that the Cole-Cole plot of red wine consists of a semicircle at frequencies above 1 GHz and a 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 Cole-Cole plots measured for seven kinds of red wines made from the same brand of Merlot in different production years, we estimated Debye dispersion parameters to reveal that the alcohol concentration and ingredient property can simultaneously be evaluated from the parameters for the semicircle and straight line, respectively.

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

1. INTRODUCTION

NOWADAYS people have a lot of interest in the quantitative evaluation of taste, which is one of the five senses in humans, however its evaluation is not so easy because taste is generally caused by a chemical reaction of food materials to taste and nose cells. As regards alcoholic drinks, on the other hand, quality that guarantees their taste 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 labor. As for rice wine or Japanese sake, measurement of the complex permittivity was conducted at millimetre wave frequencies during the fermentation process to reveal a possibility that the development of fermentation can be evaluated from the change of the permittivity [1].

For the aim of evaluating the quality of red wine, we previously measured the complex relative permittivity in the frequency range 10 MHz to 6 GHz with a network analyzer and estimated the Cole-Cole plot parameters of red wine. According to our findings the alcohol concentration of red wine can be estimated from the parameters for semicircle dispersion in the Cole-Cole plot having Debye type dispersion characterstics with a single relaxation time constant. Other ingredients can also be evaluated by the parameters for straight line dispersion [2], [3]. The developed method allows to simply estimate the concentration of alcohol in drinks containing various flavour substances (ingredients) like in the wine. No fractional distillation is necessary for the 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. METHODS

Fig.1 shows a setup for measuring complex permittivity with a network analyzer and 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 [3]. The complex relative permittivity of red wine including conductive impurities [4]-[7] can be expressed as

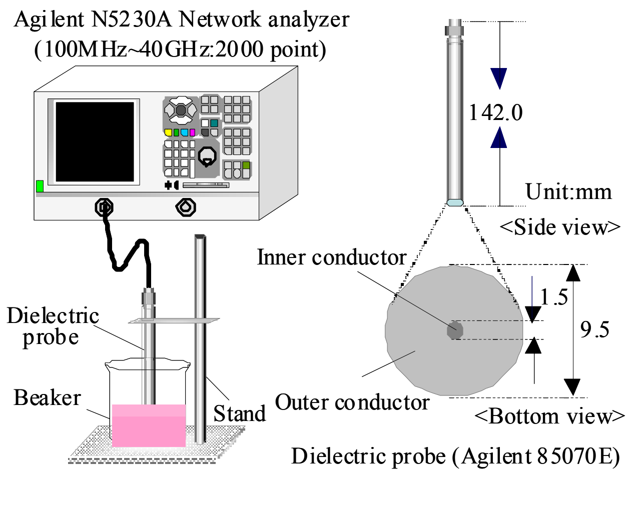

Fig.1 Setup and configuration of dielectric probe for measurement of complex permittivity

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

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. These parameters are called Debye dispersion parameters or Cole-Cole parameters. 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. [3], 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 [3].

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, and examined how the 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

Fig.2 shows the Cole-Cole plots measured and calculated for pure water, wine A, its distillation and residue. Solid lines in the figure show calculated Cole-Cole plots from Eq.(1). Tab.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. Fig.2 shows 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 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.

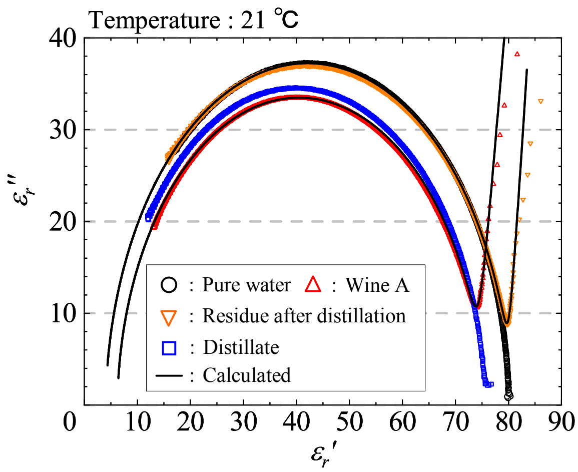

Fig.2 Measured and calculated Cole-Cole plots

Tab.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
Residue	79.5	4.0	0.986	9.64	33.50	898	0.930
Distillate	75.5<12.1>	4.9	0.983	12.61			

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

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

Merlot wine							
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 [%]

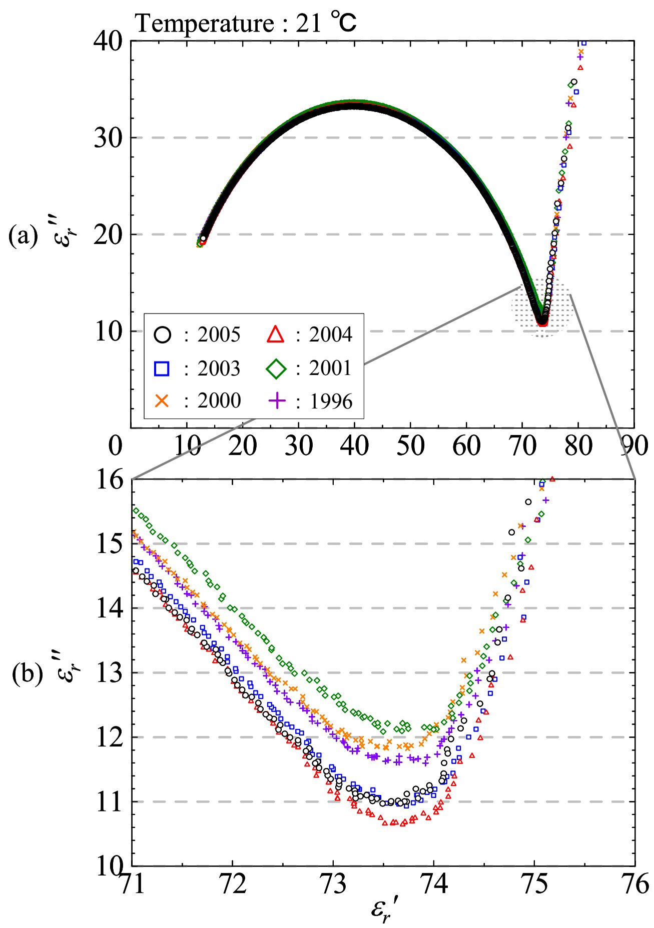

Fig.3 (a) Measured results of Cole-Cole plots for red wines of different production years and (b) enlargement of the Cole-Cole plots around minimum values

Fig.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 values. The Cole-Cole parameters in Eq. (1) were also obtained so that the calculated Cole-Cole plots agree with the measured results, which are summarized in Tab.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 wines B to G despite different production years. There are some differences between their minimum values and gradients of straight lines for the production years.

Fig.4 shows the dependence of the Cole-Cole parameters on elapsed years from the production year of red wine, which demonstrates that the dispersion parameters of ε_{r0}, $\varepsilon_{r\infty}$, τ_0 and β determining semicircles are kept almost constant with respect to elapsed years, while the parameters of τ, α and f_m for straight lines fluctuate with elapsed years, though specific relationships between these parameters and elapsed years were not observed. The latter finding, nevertheless, suggests a possibility that ingredients peculiar to red wine could be evaluated from the corresponding Cole-Cole parameters: τ, α and f_m.

4. CONCLUSIONS

Our comparison of the Cole-Cole plots for red wine, its distillate and residue 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.

Of particular interest for practical utilizations of our measurements to the end wine users and/or for wine producers is the dependence on elapsed production years of the Cole-Cole parameters, which implies a possibility that the maturity of red wine may be evaluated from the dispersion properties of wine characterized by the straight line.

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.

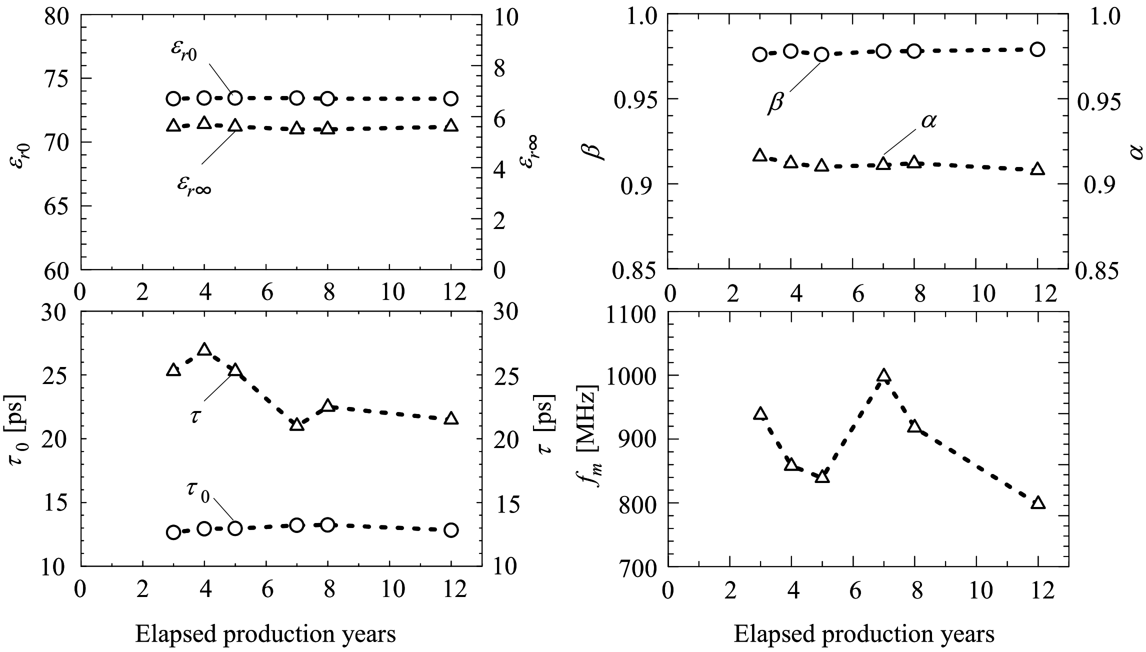

Fig.4 Dependence of Cole-Cole parameters on elapsed years

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