Multiple Transmission Method of Time Domain Spectroscopy

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A new multiple transmission method of time domain spectroscopy was developed. A small amount of the sample (0.6 cm^3) is needed in this measurement. The dielectric dispersion and absorption curves of 1-propanol, 1-butanol, and 1-pentanol have been obtained as recorder traces of the spectra stored in the minicomputer. Three dielectric parameters, ε_∞, ε_0, and τ, are estimated for these alcohols.

Time domain spectroscopy (the TDS method), which was initially proposed by Fellner-Feldegg in 1969,[1] has a great advantage over the usual frequency domain method; it can considerably reduce the time needed in obtaining continuous spectra of the dielectric constant and loss. Recently several other groups have developed various ways of measurement and analysis for the TDS method, *viz.*, the thin sample method[2,3] and the methods of lumped capacitance,[4–6] multiple reflection,[7,8] and multiple transmission.[9]

In this report, we shall describe a new measurement system for the multiple transmission method, which requires only a small amount of the sample (0.6 cm^3). The results of the measurements, using this system, of the dielectric dispersion and absorption were found to be in fair agreement with those of the preceding works.

Experimental

Principle. When an annular disk of the dielectric sample is inserted in the coaxial lines, the characteristic impedance of the line changes at Point A (Fig. 1). After having been propagated through the coaxial lines, the electromagnetic waves reach the sample, where these waves are partially reflected and partially transmitted. Suppose that the input voltage is represented by a function of the time $v(t)$, and the transmitted voltage from the disk by $r(t)$. The total transmission coefficient $S(\omega)$ at a given angular frequency, ω, will be expressed in terms of Fourier transforms of $v(t)$ and $r(t)$ as follows:

$$S(\omega) = \frac{\int_0^\infty r(t)\exp(-j\omega t)\,\mathrm{d}t}{\int_0^\infty v(t)\exp(-j\omega t)\mathrm{d}t}. \tag{1}$$

On the other hand, $S(\omega)$ is related to the dielectric constant of the sample, $\varepsilon(\omega)$, by the following formula:[10]

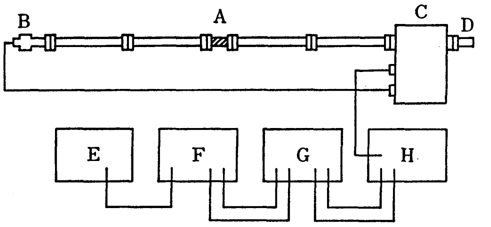

Fig. 1. Block diagram of the measurement system.
A: Sample cell, B: pulse generator, C: sampler, D: 50Ω termination, E: recorder, F: minicomputer, G: interface, H: sampling oscilloscope.

$$S(\omega) = \frac{(1-\rho^2(\omega))\exp(-(\omega l/c)j\sqrt{\varepsilon(\omega)})}{1-\rho^2(\omega)\exp(-(2\omega l/c)j\sqrt{\varepsilon(\omega)})}, \tag{2}$$

where $\rho(\omega)$ is the reflection coefficient of the air-dielectric interface and is given by $(1-\sqrt{\varepsilon(\omega)})/(1+\sqrt{\varepsilon(\omega)})$, and where l is the thickness of the sample, and c, the velocity of light.

Apparatus. The main instruments for measurements and analyses are: (a) the Hewlett-Packard 180 TDR system with a 28 ps pulse generator, (b) GR 900-L30 precision air lines, and (c) the Melcom 70 minicomputer. The sampling oscilloscope in the system was modified in such a way as the time base could be swept externally. The measurement system used in the present work is shown schematically in Fig. 1.

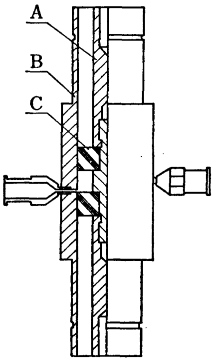

Fig. 2. Cross section of a dielectric specimen-holder.
A: Inner conductor (outer diam. 0.6204 cm), B: outer conductor (inner diam. 1.4288 cm), C: Teflon window (outer diam. 1.43 cm, inner diam. 0.43 cm, thickness 0.50 cm).

Details of Part A in Fig. 1 are shown in Fig. 2. The inner and outer conductors are the precision inner conductor rod (GR 900-9508) and the outer conductor tube (GR 900-9509), respectively. The thickness of the sample cell is 5.00 mm, and its volume is about 0.6 cm^3. The inner conductor is undercut to minimize the reflection at the surface of the Teflon. The cell is connected with the measurement system by means of two GR 900 BT precision connectors.

Measurements and Analyses. The two wave forms, $v(t)$ and $r(t)$, recorded by the oscilloscope are sampled at equal intervals along the time axis, and stored in the core memory of the minicomputer. The two signals relating to $v(t)$ and $r(t)$ are obtained when the cell is empty and when it is filled with the sample, respectively. The number of sampling points is about 1024, and the sampling interval, about 5 ps.

In order to analyze the data, the transmitted signal, $r(t)$, should have the same time origin as the input signal, $v(t)$. A set of five data-points is chosen for this reason from the steepest part of the transient, either $v(t)$ or $r(t)$, and a least-squares approximation is applied to fit the set of data to a straight line. The point at which this straight line intersects the voltage base-line is assumed to be the time reference point.

The Fourier transforms of $v(t)$ and $r(t)$ were obtained by the Samulon method.[11] The results of calculation, however, sometimes become unsatisfactory when the iteration procedure is employed in solving a complicated function such as Eq. 2. In such a case, different damping factors were used for the real and imaginary part — for example, 1.0 for the real part and 0.3 for the imaginary part; then consistent and converged values were obtained for all calculations.

To determine the limiting high- and low-frequency dielectric constants ε_∞, ε_0, and the relaxation time τ, the Debye equation,

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \tag{3}$$

was fitted to the data by the least-squares method.

All the calculations were carried out by using a Melcom 70 minicomputer and programs written in an assembler language.

Results and Discussion

Figure 3 shows an example of the input and transmitted signals observed for 1-propanol at room temperature. Each signal was an average of thirty-two scans. This average procedure reduced the jitter noise generated by the measurement system.

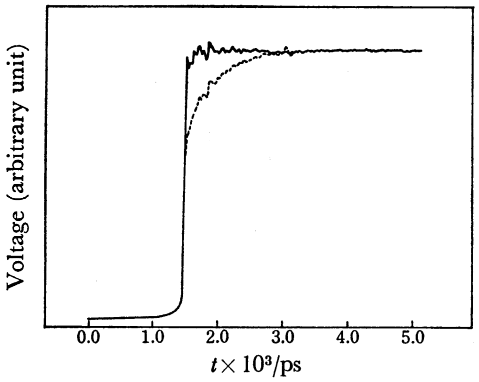

Fig. 3. Changes of the input (——) and transmitted voltages (-----) with time, t.

From Fig. 3, the dielectric dispersion and absorption spectra are obtained (see the upper curves in Fig. 4). All the curves shown in Fig. 4 are direct recorder traces of the spectra stored in a minicomputer.

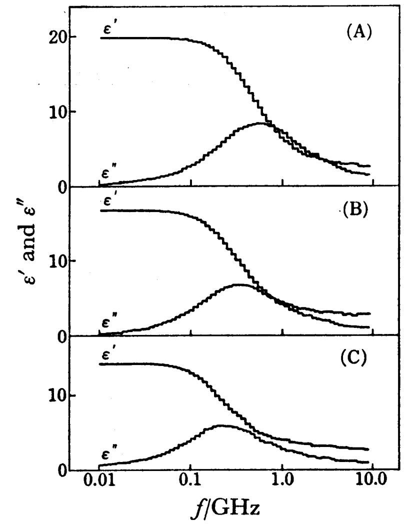

Fig. 4. Recorder traces of dielectric dispersion, ε' and absorption, ε'' spectra *vs.* frequency, f.
(A) 1-Propanol, (B) 1-butanol, (C) 1-pentanol.

It has been reported that aliphatic normal alcohols show the second and third dielectric dispersions in the high frequency region.[12] The single Debye equation, however, was fitted to our data in the 0.1—2.5 GHz frequency region to obtain the limiting high- and low-frequency dielectric constants, ε_∞, ε_0, and the relaxation time, τ, because our measurement values were not so accurate as to give many parameters in the Budo equation.[13] The ε_∞, ε_0, and τ values for 1-propanol obtained are summarized in Table 1, together with the literature values. The dielectric measurements were also carried out on 1-butanol and 1-pentanol. The ε_∞, ε_0, and τ values obtained for these alcohols are recorded in Table 2.

TABLE 1. THE LIMITING HIGH- AND LOW-FREQUENCY DIELECTRIC CONSTANTS, ε_∞ AND ε_0, AND RELAXATION TIME, τ, FOR 1-PROPANOL

	This work	Literature
ε_0	20.3	20.6,[a,b,c,e] 20.5[d]
ε_∞	2.9	4.3,[a] 3.9,[f] 3.7,[c] 3.6,[d] 3.4,[e] 3.0[b]
τ/ps	317	360,[d] 340,[f] 332,[c] 330,[b] 325[a]

a) M. J. C. Gemert, Ref. 10. b) A. Suggett *et al.*, *Nature*, **228**, 456 (1970). c) T. S. Clarkson *et al.*, Ref. 8. d) H. Fellner-Feldegg, Ref. 2. e) S. S. Stuchly *et al.*, Ref. 5. f) T. Koshii *et al.*, *Bull. Chem. Soc. Jpn.*, **47**, 618 (1974).

TABLE 2. THE LIMITING HIGH- AND LOW-FREQUENCY DIELECTRIC CONSTANTS, ε_∞ AND ε_0, AND RELAXATION TIME, τ

	Substance	
	1-Butanol	1-Pentanol
ε_0	17.4	14.9
ε_∞	3.0	3.2
τ/ps	429	665

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References

1) H. Fellner-Feldegg, *J. Phys. Chem.*, **73**, 616 (1969).
2) H. Fellner-Feldegg, *J. Phys. Chem.*, **76**, 2116 (1972).
3) A. H. Clark, F. A. Quickenden, and A. Suggett, *Trans. Faraday Soc.*, **11**, 1847 (1974).
4) M. F. Iskander and S. S. Stuchly, *IEEE Trans. Instrum. Meas.*, **IM-21**, 425 (1972).

5) S. S. Stuchly, M. A. Rzepecka, and M. F. Iskander, *IEEE Trans. Instrum. Meas.*, IM-**23**, 56 (1974).

6) M. A. Rzepecka and S. S. Stuchly, *IEEE Trans. Instrum. Meas.*, IM-**24**, 27 (1975).

7) A. M. Nicolson and G. F. Loss, *IEEE Trans. Instrum. Meas.*, IM-**19**, 377 (1970).

8) T. S. Clarkson and G. Williams, *Chem. Phys. Lett.*, **34**, 461 (1975).

9) B. Gestblom and E. Noreland, *J. Phys. Chem.*, **81**, 782 (1977).

10) M. J. C. Gemert, *Philips Res. Repts.*, **28**, 530 (1973).

11) H. A. Samulon, *Proc. I.R.E.*, **37**, 10 (1949).

12) S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, **69**, 1294 (1965).

13) A. Budo, *Phys. Z.*, **39**, 706 (1938).