Technique for measuring the frequency-dependent complex dielectric constants of liquids up to 20 GHz

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A technique for the measurement of the frequency-dependent complex dielectric constant \( \varepsilon = \varepsilon' - j\varepsilon'' \) of liquids applicable to frequencies up to at least 20 GHz is described. The technique utilizes a coaxial probe dipped into the liquid. The reflection coefficient of the probe was measured using a network analyzer between 45 MHz and 20 GHz. A new de-imbedding procedure for eliminating the connector and coax mismatches is described, during which the impedance \( Z(\varepsilon) \) of the probe end was determined. The dielectric constant \( \varepsilon \) was determined from \( Z(\varepsilon) \) by modeling the coax–liquid interface as a capacitance. The de-imbedding procedure, which utilizes three calibrations, directly eliminates the (unknown) fringe-field impedance. Radiation effects were minimized by using narrow (0.047-in.) semirigid coax. The technique yields accurate results for \( \varepsilon' \) and \( \varepsilon'' \) of liquids such as methanol and water over the entire frequency range up to 20 GHz, and can be used to determine the relaxation spectra of liquid and liquidlike samples.

INTRODUCTION

There are few systematic measurements of the dielectric properties of condensed matter above 10 MHz which cover a broad frequency range. Techniques which utilize resonant structures in the microwave frequency range, while they possess the required sensitivity, are limited to a very narrow range of frequencies. Recently, the availability of network analyzers which are able to measure the characteristics of transmission lines over a broad frequency range as high as 26 GHz have raised the prospect of measurements using coaxial techniques.

In this article, we describe the experimental techniques and the requisite analysis for measuring the complex dielectric constants \( \varepsilon = \varepsilon' - j\varepsilon'' \) of liquids. The method is also applicable to samples of similar nature—colloids, solutions, etc. The method basically involves determination of the complex impedance from measurements of the reflection coefficient of a simple sample cell, which essentially consists of a coaxial semirigid cable terminated by the liquid sample. The complex impedance, measured at the network analyzer plane, is de-imbedded to deduce the sample impedance, and from it, the dielectric constant of the liquid. We model the liquid–coax interface as an impedance \( Z(\omega, \varepsilon) = [\frac{\mu L}{\omega C'} + \frac{j\omega C''}{\varepsilon}]^{-1} \). The de-imbedding, which requires calibrations with specific terminations, eliminates connector impedances and any other line mismatches, and also importantly the fringe-field capacitance \( C' \) within the coax, and the capacitance parameters \( C_m \) all of which are frequency dependent and hard to measure. The three calibration terminations are open, a short using liquid mercury, and a standard liquid such as acetone.

The method has successfully been applied to measurements of \( \varepsilon \) for a variety of liquid samples, up to 20 GHz. Using either a 0.085- or 0.047-in.-diam semirigid coaxial cable, the technique gives accurate results (errors less than 2%) for low dielectric constant liquids (\( \varepsilon' < 30 \)), over the entire frequency range from 45 MHz to 20 GHz. In addition to test liquids such as methanol, toluene, etc., we have also studied solutions of polymers and DNA with this technique.

For higher dielectric constant liquids such as water, radiation effects become rapidly important, particularly with increasing frequency. The narrower (0.047-in.) probe was necessary to minimize radiation effects. With this probe, results accurate to 5% are obtainable up to 20 GHz for water. We are thus able to observe the relaxation spectrum of water.

We find that application of the technique requires considerable care regarding calibrations—however, once the proper procedures, which are described, are followed, the results are entirely reproducible. The techniques are easily extended to study the temperature dependence of the dielectric constants. We are presently involved also in extending the methods to the case of solid samples.

I. MEASUREMENT CONFIGURATION

The measurement configuration is as shown in Fig. 1. A semirigid coaxial cable, of size 0.141, 0.085, or 0.047 in., with an SMA connector on one end and a flat face on the other, is dipped into the liquid. The connector end is mated to an HP 8510 Network Analyzer—since the dominant length of the coax is required to be vertical, the mating to the ANA was made either with a right-angle adapter, connector, or bend in the coax.

The HP 8510 system used consists of an HP8510B analyzer, an HP8513A reflection/transmission test set usable from 45 MHz to 26 GHz. The source is a HP 8341B synthesizer sweeper, operating between 10 MHz and 20 GHz. The sweeper was used in the step mode over the desired frequency range, with typical selections of 51–201 points. We have found that a synthesized source, and its operation in a step mode, resulting in good phase stability, is essential to obtaining reproducible data free of spurious oscillations.

A personal computer (PC AT) was set up to receive pairs of data [Re and Im(\( \rho \)) for each frequency point] over.
an IEEE-488 bus and used for subsequent numerical analysis.

The procedure for experimental data collection is described below step by step.

**A. Open**

With the coax terminated by free space, the measurement plane of the ANA was moved to the coax end using the electrical delay provided. The delay, which corresponds to the length of the coax (typically 6–12 in.), was adjusted to give a cluster of points near the $\Re(\rho) = 1$, $\Im(\rho) = 0$ point, at the middle of the right-hand side of the display. Because of connector and line mismatches, the cluster is not a point, but can occupy a region. The pairwise $\rho_A$ data were read into the computer.

**B. Short**

A short at the coax end was created by raising a small vessel (about 6 cc) filled with mercury, until the coax end was well within the liquid. This resulted in a cluster of points around the position $[\Re(\rho) = -1$, $\Im(\rho) = 0]$, at the middle of the left-hand side of the display. The pairwise data $\rho_B$ were again read into the computer.

**C. Standard liquid**

The mercury cell was removed. At this point, the display was checked to ensure that the data returned to the configuration for an open. A cell (of volume typically $< 10$ cc) with a standard liquid, usually acetone, was now inserted so that the coax end was well immersed in the liquid. The data $\rho_C$ were again read into the computer.

**D. Sample liquid**

The standard liquid was removed, and time was allowed for the acetone to evaporate completely from the end of the coax, until the display returned to the open configuration. The procedure was repeated with the liquid sample, and data $\rho_M$ were collected.

We emphasize that the above procedure of three calibration measurements and a sample measurement were taken with minimal disturbance, and without disconnecting the connectors.

**II. ANALYSIS: DE-IMBEDDING OF SAMPLE IMPEDANCE**

The “open,” short, and standard liquid data are used for computerized calibration based on the equivalent circuit given in Fig. 2(a). By properly modeling $Z(\omega, \epsilon)$ ( $\epsilon$ is the dielectric constant of the fluid surrounding the probe end) of the end of the coax, we can extract three parameters, $\Delta$, $\Delta_{12}$, and $\Delta_{23}$, which are related to $Z_1$, $Z_2$, and $Z_3$, and then we obtain the dielectric constant of the sample liquid.

The calibration procedure of consecutively placing three known terminations, a short circuit, an open circuit, and a matched load at the reference plane of a network analyzer, can significantly improve the accuracy of a network analyzer measurements. In our measurement configuration shown in Fig. 1, which is a very convenient way to measure liquid samples, the network analyzer calibration alone cannot eliminate the effects of the connectors and the coax probe. This is shown in Fig. 3, where we plot $\epsilon'$ and $\epsilon''$ for water determined with the ANA calibration only (+ ‘s) and with the calibration procedure described here below (O’s), for the 0.047-in. probe. Without the procedure and analysis described in this article, it is difficult to determine the capacitance parameter $C_m$, and hence to get accurate results, as is obvious from Fig. 3. Clearly the ANA calibration alone is inadequate, and leads to oscillations and large inaccuracies, which we attribute to the connector mismatches and indeterminate parameters, as we discuss later.

Various kinds of calibration techniques for one-port measurements have been developed and used for measurements that cannot be carried out at the reference plane of a network analyzer.$^{5,6}$ For measurements using a semirigid coax probe, the proper modeling of the frequency $\omega$ and sample...
dielectric constant $\varepsilon$-dependent impedance $Z(\omega, \varepsilon)$ of the probe end is crucial.\textsuperscript{5,2} The calibration technique we use, which examines the problem from a new point of view, eliminates uncertain factors such as fringe-field (complex, frequency-dependent) capacitance and the frequency dependence of the probe parameters, as shown below.

For a TEM mode propagating along a transmission line with characteristic resistance $Z_0$, its output can be completely determined by three parameters. It can be easily shown that the output of the TEM mode propagating through two transmission lines which have different characteristic impedances can also be similarly determined. Since the complicated linear microwave transmission system with coax and connectors can be regarded as the combination of many pieces of coax with different characteristic impedances, we need to determine three parameters at each measuring frequency. We use the equivalent circuit in Fig. 2(a) with $Z_A$, $Z_B$, and $Z_C$ to characterize the transmission line and $Z(\omega, \varepsilon)$ for the impedance of the end of the probe.

$Z_M(\omega, \varepsilon)$ is the measured output impedance which can be obtained from the complex reflection coefficient

$$\rho_M = \Gamma e^{-i\phi}$$

measured by the 8510 ANA, and

$$Z_M = Z_0 \frac{1 + \rho_M}{1 - \rho_M}.$$  \hspace{1cm} (2)

$Z_M$ also can be expressed from Fig. 2 for every frequency:

$$Z_M = Z_1 + \frac{Z_2[Z_4 + Z(\varepsilon)]}{Z_5 + Z_3 + Z(\varepsilon)}.$$  \hspace{1cm} (3)

Equation (3) is equivalent to

$$\Delta' + \Delta_1 Z_1 Z(\varepsilon) - \Delta_2 Z_M Z(\varepsilon) = Z_M Z(\varepsilon),$$

where

$$\Delta' = Z_1 Z_2 + Z_3 Z_5 + Z_3 Z_4,$$

$$\Delta_1 = Z_1 + Z_2,$$

$$\Delta_2 = Z_3 + Z_5.$$  \hspace{1cm} (4)

By properly modeling the end of the probe, that is, by knowing the way in which $Z$ depends on frequency $\omega$ and the dielectric constant $\varepsilon$ of the surrounding medium

$$Z(\omega, \varepsilon) = f(\omega, \varepsilon),$$

we can get $Z(\omega, \varepsilon)$ from known $\varepsilon(\omega)$ and vice versa.

Therefore, if we first put three calibration media with known $\varepsilon_A$, $\varepsilon_B$, and $\varepsilon_C$ and take the reflection coefficient measurements $\rho_A$, $\rho_B$, and $\rho_C$, we can get $Z_{MA}$, $Z_{MB}$, and $Z_{MC}$ from (2), and $Z_A$, $Z_B$, and $Z_C$ from (8). Equation (4) gives three equations which contain three unknown parameters, $\Delta'$, $\Delta_1$, and $\Delta_2$:

$$\Delta' + \Delta_1 Z_1 Z_A - \Delta_2 Z_{MA} = Z_{MA} Z_A,$$

$$\Delta' + \Delta_1 Z_1 Z_B - \Delta_2 Z_{MB} = Z_{MB} Z_B,$$

$$\Delta' + \Delta_1 Z_1 Z_C - \Delta_2 Z_{MC} = Z_{MC} Z_C.$$  \hspace{1cm} (5)

The parameters $\Delta'$, $\Delta_1$, and $\Delta_2$ can be calculated from the above equations for each frequency, and substituted into Eq. (4) to get $Z(\varepsilon)$ for the sample medium:

$$Z(\varepsilon) = \frac{\Delta' - \Delta_1 Z_M(\varepsilon)}{Z_M(\varepsilon) - \Delta_2}.$$  \hspace{1cm} (6)

where $Z_M(\varepsilon)$ is obtained from the measured reflection coefficient $\rho_M$ according to Eq. (2). Then, from relation (8), we obtain the dielectric constant of the sample, as discussed next.

### III. Modeling of Coax Termination: Fringing Effects

Generally, the coax terminated by a medium filling the other half-space can be described by the equivalent circuit given in Fig. 2(b), which represents the $\varepsilon$- and $\omega$-dependent complex capacitance due to the fringing field.\textsuperscript{3,8} We have

$$Z(\omega, \varepsilon) = \left[ j\omega C(\omega, \varepsilon) + G(\omega, \varepsilon) \right]^{-1},$$

$$= \left[ j\omega C_f(\omega) + j\omega C_0(\omega) \right]^{-1}.\hspace{1cm} (3a)$$

When $\sqrt{\varepsilon_A/\lambda}, \sqrt{\varepsilon_B/\lambda} \ll 1$, we can approximate\textsuperscript{3,8,9}

$$C(\omega, \varepsilon) = C_f(\varepsilon).\hspace{1cm} (3b)$$

$C_f$ represents the fringe-field effects inside the probe, and $C_0$ the fringe-field coupled to the sample. The effect of $C_f$ can be included into the three network parameters, as in Fig. 2(c). Therefore, the Eqs. (9)–(11) for calibration and Eq. (4) for the measurement can be written as

$$\Delta' + \Delta_1 \varepsilon_A + \Delta_2 Z_{MA} = \frac{Z_{MA}}{\varepsilon_A},$$

$$\Delta' + \Delta_1 \varepsilon_B + \Delta_2 Z_{MB} = \frac{Z_{MB}}{\varepsilon_B},$$

where

$$\Delta_1 = \frac{Z_2[Z_4 + Z(\varepsilon)]}{Z_5 + Z_3 + Z(\varepsilon)}.$$  \hspace{1cm} (7)
\[ \Delta + \frac{\Delta_{12}}{\epsilon_C} + \Delta_{23}Z_{MC} = \frac{Z_{MC}}{\epsilon_C}, \]
\[ \Delta + \frac{\Delta_{12}}{\epsilon} + \Delta_{23}Z_M = \frac{Z_M}{\epsilon}. \]

Solving (14)–(16), we get the values for \( \Delta, \Delta_{12}, \) and \( \Delta_{23} \), and substituting them into (17), we get
\[ \epsilon = \frac{Z_M - \Delta_{12}}{\Delta + Z_M \Delta_{23}}. \]

Note that the measurement does not depend on any information of the fringing capacitance. Also the frequency dependent parameter \( C_0(\omega) \), which is complex, is implicitly determined at every measurement frequency by this procedure.

The procedure next requires expressions for the three calibration impedances, \( Z_A, Z_B, \) and \( Z_C \). For the short, for which we use liquid mercury, \( Z_B = 0 \). For the "open," in which the probe is in air, we use Eq. (14) with \( \epsilon' = 1 \) and \( \epsilon'' = 0 \). For the standard, which is usually acetone, Eq. (16) is used with a Debye model for \( \epsilon \):
\[ \epsilon = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{(1 + j \omega \tau)}, \]
with parameters obtained from the literature, \( \epsilon_0 = 21.2, \epsilon_\infty = 1.9, \) and \( \tau = 3 \times 10^{-12} \) s.

The results of using the above procedure are shown in Fig. 3 for water as a sample liquid. Also shown in Fig. 3 are the data taken only using the calibration at the right-angle adapter end, choosing \( C_r = 0 \) and \( C_0 = 0.8 \times 10^{-14} \) F. The improvement using the present procedure is clearly evident. In particular, the unwanted oscillations present using the ANA calibration only are eliminated by the three-standard calibration described here. The oscillations are due to the connector mismatch, which is not accounted for using the machine calibration only, but requires an actual calibration at the measurement plane. (We note that in Ref. 4, a time-domain gating was utilized to reduce the effect of connector mismatch. The present technique does not require such a time-domain procedure.) Also the machine calibration alone does not yield the important parameters \( C_0 \) and \( C_1 \), for which either approximate estimates\(^5\) or measurements\(^6\) are required. However, as is evident from the analysis above, the three-standard calibration procedure and analysis of this article, eliminates \( C_0 \) and \( C_1 \), and provides an accurate representation of the true frequency dependence of liquid samples.

Some structure at low frequency is evident in Figs. 4 and 5 for data taken by 0.141-in. probe. It is a manifestation of a "container" effect. This arises due to the fact that the liquid volume in the container acts as a dielectric-filled resonant cavity with resonant frequency less than 5 GHz for liquids with \( \epsilon' \approx 30-100 \). We have experimentally verified this by varying the height of the liquid and noting that the resonance shifts accordingly. The "container" or finite-volume effect can be almost completely eliminated by using a large of liquid volume relative to probe size such as for the 0.047-in. probe. Yet another possible solution to this problem is to experimentally dampen this resonance and reduce the \( Q \) to be much less than 1.

![Fig. 4. Frequency dependence of \( \epsilon' \) and \( \epsilon'' \) for methanol taken with a thick 0.141-in. probe (×'s) and thin 0.085-in. probe (+'s). The solid line represents the Debye response for methanol.](image)

**IV. DISCUSSION OF RESULTS: RADIATION EFFECTS AND ERRORS**

Figure 4 presents the data for \( \epsilon' \) and \( \epsilon'' \) for methanol between 45 MHz and 20 GHz obtained using the technique described above. Data taken with a thick 0.141-in. (×'s) and a thin 0.085-in. (+'s) probe are shown. Results with

![Fig. 5. Frequency dependence of \( \epsilon' \) and \( \epsilon'' \) for de-ionized water taken with a thick 0.141-in. probe (+'s), 0.085-in. probe (×'s), and a 0.047 in. probe (○'s). The difference between the probes is due to radiation effects which are minimized in the thinnest probe.](image)
the two sizes of probes agree fairly well, with the only discrepancies appearing at higher frequencies for \( \varepsilon'' \). For comparison, the Debye form Eq. (19) is also shown with parameters \( \varepsilon_0 = 33.64, \varepsilon_\infty = 5.7, \) and \( \tau = 53 \times 10^{-12} \) s, taken from Ref. 10. This form is expected to apply with good accuracy to methanol, and the data are in fair agreement with it.

For water, the data for \( \varepsilon' \) and \( \varepsilon'' \) as functions of frequency are shown in Fig. 5, both for the thick 0.141-in. probe (\( \times \)'s), a thinner 0.085-in. probe (\( \circ \)'s), and a very narrow 0.047-in. probe (\( \bigcirc \)'s). Here, the effects of radiation are dramatically evident in the difference in data between the three probes.

The effects of radiation can be modeled as a lossy conductance \( G(\omega) \) in parallel with a capacitance \( B \), viz. 
\[
joC(\omega_\varepsilon) = jB(\omega_\varepsilon) + G(\omega_\varepsilon).
\]

To first order,\(^{8,12}\) the conductance \( G \propto (b^2 - a^2)^2\omega^2\varepsilon^2 \), where \( a \) and \( b \) are, respectively, the outer and inner diameters of the coax probe. Thus, the effects of radiation drastically increase with probe size, frequency, and dielectric constant of the liquid. The differences between the thick probe and thin probe results of Fig. 5 are entirely due to the probe size and the larger dielectric constant of the liquid, and increase with increasing frequency. The thinnest probe greatly minimizes the effects of radiation.

At 45 MHz, \( \varepsilon' \) is measured to be 79.3, which compares very well with the value obtained from the temperature-dependent expression \( \varepsilon_0 = 87.740 - 0.40087T + 9.378 \times 10^{-14}T^2 \) at 22 °C given in Ref. 13. The frequency-dependent data obtained using the 0.047-in. probe was fit to a Debye expression, with \( \varepsilon_0 = 79.3, \varepsilon_\infty = 4.7, \) from which the dielectric relaxation time was deduced to be \( \tau = 9.0 \pm 0.5 \) ps. As Fig. 6, which presents a comparison of the data and the Debye expression, shows, the data for water can be quite adequately described by a Debye relaxation with a single relaxation time, a conclusion which agrees well with that of Refs. 13 and 14. Our data provides an accurate estimate of the relaxation time (which is determined by the viscosity and hence is temperature dependent), and the measured value agrees with other values in the literature. We note that in contrast to other estimates of the relaxation time, which rely on spot frequency measurements or on compilations of data from different experiments, the technique presented here directly finds almost the complete relaxation spectrum of water.

**Error analysis.** Analysis shows that the instrument accuracies contribute negligibly (less than 0.1%) to the accuracy of measurement.

The principal source of error is caused by the termination modeling. The calibration procedure eliminates the error in determining the capacitance parameters \( C_f(\omega) \) and \( C_0(\omega) \). Residual errors are due to ignoring higher orders of \( \omega T \) in \( B(\omega_\varepsilon) \) and the radiation conductance \( G(\omega_\varepsilon) \) (13a).

We estimate the error introduced by these higher order corrections as\(^{8,12}\)

\[
\frac{\Delta \varepsilon}{\varepsilon} \approx \left[ B(\omega_\varepsilon) - \sqrt{\varepsilon_0 C} - jG(\omega_\varepsilon) \right] / \sqrt{\varepsilon_0 C}
\]

\( C \) is a constant.

This gives \( \Delta \varepsilon/\varepsilon < 4\% \) for methanol over the entire frequency range up to 20 GHz for the 0.047-in. probe. For water for the 0.047-in. probe, \( \Delta \varepsilon/\varepsilon < 5\% \) up to 6 GHz and \( < 10\% \) between 16 and 20 GHz. These errors must be regarded as upper bounds, and the actual errors are much smaller.

**Calibration standards.** The method obviously relies on accurate and reliable calibration standards and their modeling. The open and short calibrations are quite reliable and accurate. (Care must be taken with the use of liquid mercury, since it corrodes the metallic coax. On occasion we have found that the use of an ultrasonic cleaner greatly improves the measurement.) We have preferred acetone as a standard liquid, because it is easily available in pure form, has a reasonable dielectric constant, and exhibits little dispersion in the present frequency range. The parameters used in the Debye form for acetone are fairly accurate. At present the errors due to the calibration standards are much less than those due to the modeling of the liquid-coax interface.

**V. DISCUSSION**

We have presented a method for the measurement of the complex dielectric constant of liquids and liquidlike samples, using a coaxial probe between 45 MHz and 20 GHz. Impedances are measured using a HP 8510 network analyzer. Three calibration standards are utilized, which are usually an open, short, and a standard liquid. The calibrations enable the elimination of connector and line mismatches, and an analysis was developed to de-imbed the impedance of the liquid–probe interface, from which by proper modeling the sample dielectric constant is extracted. The de-imbedding procedure eliminates the unknown fringe-field impedance parameters \( C_f \) and \( C_0 \) at each measurement frequency.
The accuracy of the modeling determines the accuracy of the dielectric constant measurements. The method gives accurate results for liquids such as methanol and water up to 20 GHz provided narrow (0.047-in.) coax probes are used to minimize radiation.

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1S. Sridhar, Microwave J. 1987, 118 (June 1987).
2Manufactured by Hewlett-Packard Co., Palo Alto, CA.