Permittivity Measurements Using Open-Ended Sensors and Reference Liquid Calibration—An Uncertainty Analysis

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Abstract—**Results of the uncertainty analysis of the error-corrected permittivity measurements of materials using open-ended sensors are reported. Uncertainties in the permittivities of the reference liquids due to the uncertainties in the Cole-Cole parameters are discussed. The effect of the selection of these parameters of reference liquids, when used as calibration standards for error-corrected permittivity measurements, is highlighted. Measurements are performed on 15 and 30 ppt saline and the results are presented along with the measurement uncertainties resulting from uncertainties in Cole-Cole parameters of the reference liquids.**

I. INTRODUCTION

VARIOUS sensors based on coaxial transmission lines and waveguide structures have been used in the past to measure the dielectric properties of the materials. The open-ended sensors proved to be very useful due to a relatively minor constraints on the test material shape and configuration. With one-port error-correction, using reference liquids as calibration standards, it is possible to calibrate the open-ended sensors accurately. Low uncertainties in the permittivity measurements can be achieved by proper selection and characterization of the reference liquids. A critical study of the uncertainties in the error-corrected permittivity measurements due to the uncertainties in the characterization of the reference liquids and the selection reference liquids as calibration standards is presented in this paper.

It is possible to reduce the uncertainties of the permittivity measurements with the open-ended sensors by using a proper calibration technique. A convenient and relatively accurate liquid calibration method, was proposed by Kraszewski *et al.* [1]. In this technique all measurements were performed by placing the standards and unknown (a short circuit, an open circuit, a reference liquid and an unknown dielectric material) at the end of the probe. The standard one-port, three-term error correction was then applied to the measured data to determine the permittivity of the unknown material [2]. A detailed comparison was also given between the proposed calibration technique and the calibration technique used earlier by Stuchly *et al.* [3]. In [3], the standard error correction was used with one modification, in which the matched termination was connected to the probe-connector plane rather than the reference plane (end of the line) during the calibration. Many other workers reported the error-corrected permittivity measurements using the liquid calibration technique [4]–[10].

In order to enhance the accuracy of the permittivity measurements, the open-ended sensor is calibrated by measuring the reflections when the probe is open-circuited, short-circuited and immersed in a reference liquid (used as a calibration standard). The accuracy enhancement depends on the accuracy with which the permittivity of the standards are known as a function of frequency and temperature. Water, saline, and methanol are usually selected as reference liquids [4]–[10]. The permittivities of these liquids, as a function of frequency and temperature, are determined by the Cole–Cole parameters. In the past, many authors estimated the Cole–Cole parameters and their uncertainties for various reference liquids, such as, water [11]–[14], saline [15]–[17] and methanol [18]. These parameters were estimated based on the actual measurements. The Cole–Cole parameters reported and used by various authors differ, making it difficult to assess the accuracy of their measurements. Hence, it is necessary to estimate the uncertainties in the permittivity of the reference liquids due to the uncertainties in Cole–Cole parameters and the resulting uncertainties in the measured values. In order to accomplish this an uncertainty analysis was performed on the error-corrected permittivity measurements. Accurate empirical formulas for the Cole–Cole parameters of water, methanol and saline were derived. The uncertainties of the permittivity of the reference liquids and the uncertainties of the error-corrected permittivity measurements, resulting from the uncertainties in the Cole–Cole parameters of water, methanol and saline are presented.

II. THEORY

Various authors used the basic error-correction technique [2] to accurately measure the permittivity of the test materials. A brief description of the principle of operation and of the standard error-correction technique is presented below.

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A. Principle of Operation

A system for the non-destructive measurement of material permittivities consists of an open-ended coaxial line sensor and an automated network analyzer (ANA). The sensor is placed in contact with the material under test and the resulting reflection coefficient is measured with the ANA. Knowledge of the relationship between the measured reflection coefficient and the material properties then allows one to determine the latter.

The geometry of open-ended coaxial line is shown in Fig. 1(a) whereas Fig. 1(b) shows the equivalent circuit. From the equivalent circuit, the terminating load admittance, is related to the reflection coefficient. Hence, if the parameters of the equivalent circuit are known the permittivity may be determined from the measured admittance.

When the open-ended coaxial lines are used for permittivity measurements, small changes of relatively large reflection coefficients should be accurately measured, thus calibration of the measuring system is critical (II-B). The procedure consists of placing three standards, which produce known reflection coefficients, at the end of the coaxial line. The commonly used standards are: an open circuit, a short circuit, and a liquid with "known" dielectric properties. Although the short and open circuits are well characterized, the uncertainties in the assumed properties of the reference liquid lead to uncertainties in the measured permittivity. The propagation of errors is examined in this paper.

B. Error Correction Technique

Due to the imperfections in the instrumentation, the measured reflection coefficient differs from the true reflection coefficient of the device under test (DUT) at the reference plane. The true reflection coefficient of the device can be determined from the measured value, when the S-parameters (S_{11}, S_{12}, S_{21} and S_{22}) of the two-port network existing between the measurement and reference planes are known. These parameters are usually determined from the measured reflection coefficients at the measurement plane, for three standards (S_i; $i = 1, 2, 3$) connected at the reference plane whose reflection coefficients (Γ_i; $i = 1, 2, 3$) are known as functions of frequency. This can be expressed as follows:

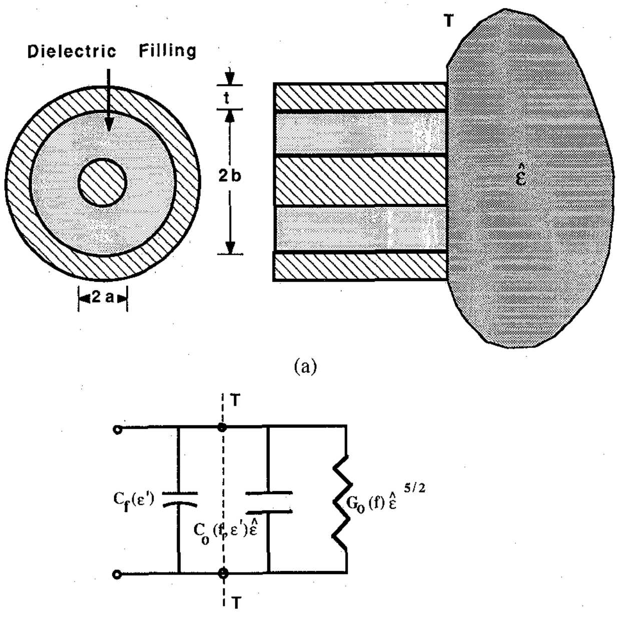
$$S_i = S_{11} + \frac{S_{12} S_{21} \Gamma_i}{1 - S_{22} \Gamma_i}; \qquad i = 1, 2, 3 \tag{1}$$

and the true value of the measured reflection coefficient of the DUT, Γ_d, is calculated from

$$\Gamma_d = \frac{S_d - S_{11}}{S_{22}(S_d - S_{11}) + S_{12} S_{21}} \tag{2}$$

where S_d is the measured (uncorrected) reflection coefficient of the DUT and S_{11}, S_{22} and $S_{12}S_{21}$ are the error coefficients which are given by

$$S_{11} = \frac{\Gamma_1 \Gamma_2 S_3 (S_1 - S_2) + \Gamma_2 \Gamma_3 S_1 (S_2 - S_3) + \Gamma_3 \Gamma_1 S_2 (S_3 - S_1)}{\Gamma_1 \Gamma_2 (S_1 - S_2) + \Gamma_2 \Gamma_3 (S_2 - S_3) + \Gamma_3 \Gamma_1 (S_3 - S_1)} \tag{3}$$



(a)

(b)

Fig. 1. Geometry of the open-ended coaxial line sensor and its equivalent circuit.

$$S_{22} = \frac{\Gamma_3(S_{11} - S_2) + \Gamma_2(S_3 - S_{11})}{\Gamma_2 \Gamma_3 (S_3 - S_2)} \tag{4}$$

$$S_{12} S_{21} = \frac{(S_2 - S_{11})(1 - S_{22}\Gamma_2)}{\Gamma_2}. \tag{5}$$

The error-correction technique discussed above can be used to de-embed the two-port network as long as the standards used for calibration are independent. In the case of a standard calibration [2], a short, an open and a matched termination are used as calibration standards. When an ideal inductor, capacitor and resistor are used as calibration standards, the error correction can transform the imperfect network analyzer to an ideal network analyzer having infinite directivity, perfect source match and a flat frequency response.

C. Uncertainties in the Reference Liquids

As was pointed above, the imperfections in the instrumentation, connector mismatches, and dispersion of the transmission line can be significantly reduced by selecting independent standards whose characteristics are known with minimum uncertainty. It is relatively easy to obtain short, open and matched terminations with standard connectors. However, for structures like open-ended sensors it is difficult to produce a good matched termination. For this reason, Kraszewski *et al.* [1] introduced a liquid as the third calibration standard, resulting in a considerable improvement in the accuracy of the permittivity measurements.

TABLE I-A
COLE–COLE PARAMETERS OF THE REFERENCE LIQUIDS (0.5N SALINE AND 1.0N SALINE) AT 25°C REPORTED IN LITERATURE

Reference Liquid	Cole–Cole Parameters	From [15]	From [20]	From (A5)
0.5N Saline	ϵ_s	69.257	69.499	69.257
	ϵ_∞	4.9	4.9	4.5
	τ(ps)	7.995	8.098	8.020
	α	0.0	0.0	0.2
1.0N Saline	ϵ_s	61.822	61.418	61.822
	ϵ_∞	4.9	5.6	4.5
	τ(ps)	7.804	7.961	7.829
	α	0.0	0.0	0.02

TABLE I-B
COLE–COLE PARAMETERS OF THE REFERENCE LIQUIDS (WATER AND METHANOL) AT 25°C REPORTED IN LITERATURE

Reference Liquid	Cole–Cole Parameters	From [11] using (A1) and (A3)	From [8] (taken from [11]	Calculated in this paper using (A2) and (A4)
Water	ϵ_s	78.197	78.5	78.3
	ϵ_∞	5.188	5.2	4.5
	τ(ps)	8.192	8.3	8.12
	α	0.0	0.0	0.02
Methanol	ϵ_s	32.616	32.6	33.7
	ϵ_∞	5.81	5.6	4.35
	τ(ps)	47.419	48.0	49.64
	α	0.0	0.0	0.043

The following substances have been frequently used as reference liquids: water, methanol, and saline. The dielectric properties of these liquids can be described by the Cole–Cole equation:

$$\hat{\epsilon} = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} - j\frac{\sigma}{\omega\epsilon_o} \quad (6)$$

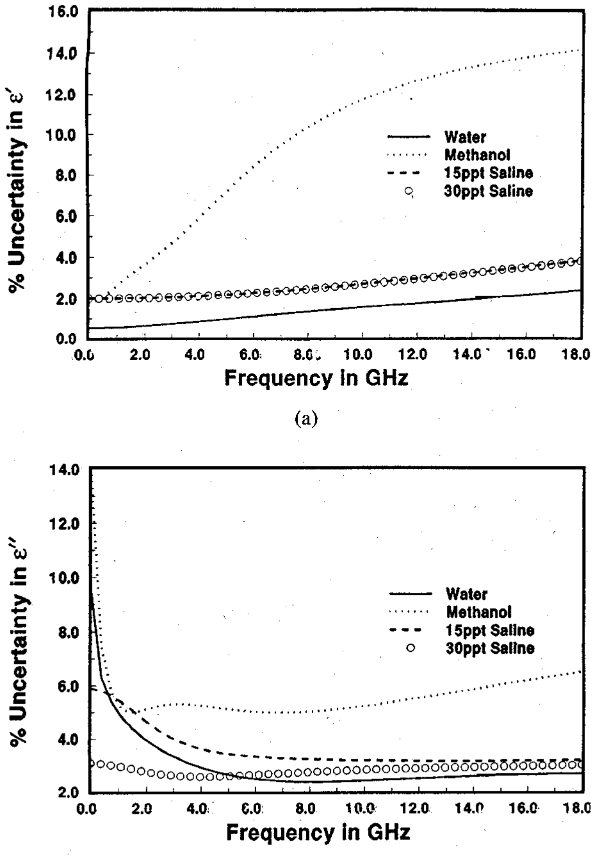
where ϵ_∞ is the optical permittivity, ϵ_s is the static permittivity, τ is the relaxation time, α is the distribution parameter and σ is the ionic conductivity of the liquids. Knowing these parameters, the permittivity of the liquids can be accurately determined. These parameters are determined from the independent accurate measurements of the permittivity at various frequencies and temperatures. The uncertainties involved in estimating these parameters are often quite high, particularly for methanol [18]. The Cole–Cole parameter data are available from different sources, for water [11]–[14], for methanol [14], [18], and for saline [15]–[17]. In most cases, the Cole–Cole parameters are tabulated as a function of temperature. When the permittivity measurements are made as a function of frequency at a particular temperature, the uncertainty involved in selecting the appropriate parameters from the tabulated data increases the error in specifying the standards characteristics. Using non-linear regression, the tabulated values of [11]–[18] were used to determine the coefficients of a 4th order polynomial for each Cole–Cole parameter. These expressions are given in the Appendix A.

Due to the differences in the Cole–Cole parameters used by different authors for calibration, it is difficult to compare the results of their work. These differences are evident in Table I which lists some previously published values and the parameters computed using the equations given in the Appendix A. The uncertainties in the permittivities of water, methanol, saline with 15 ppt and 30 ppt due to the uncertainties in Cole–Cole parameters have also been calculated as a function of frequency. The corresponding equations are given in the Appendix B. The relative uncertainties (rms) in the permittivity of the reference liquids are computed at 26°C as a function of frequency and are shown in Fig. 2.

D. Uncertainties of the Error-Correction Technique due to Reference Liquids

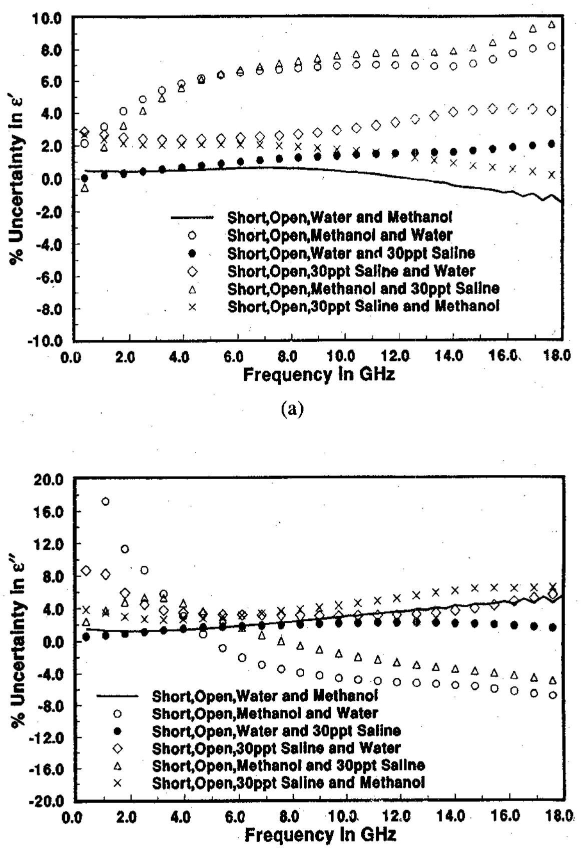
The uncertainty analysis of the permittivity measurements using reference liquid calibration is necessary for an informed selection of the proper liquid as a calibration standard. The error in the measured permittivity due to the uncertainties in the calibration liquid permittivities is difficult to visualize due to the involved calibration technique. Therefore, a simple method is used to simulate the measurement of the permittivity using error correction technique.

For this simulation, a cascade of two two-port networks is considered, one representing an imperfect network analyzer, *A* and the other representing an open-ended sensor, *P*. The open-ended coaxial line is considered here as a



(b)

Fig. 2. Relative uncertainties (rms) in the permittivities of the reference liquids (water, methanol, 15 and 30 ppt saline at 26°C) due to the uncertainties in the respective values of the Cole–Cole parameters. (a) % uncertainty in ϵ' and (b) % uncertainty in ϵ''.



(b)

Fig. 3. Relative uncertainties (rms) in the permittivity of test liquid due to the uncertainties in the Cole–Cole parameters of reference liquid used as calibration standard ($i = 3$) at 26°C. (a) % uncertainty in ϵ' and (b) 5 uncertainty in ϵ''.

Calibration Standards	Test Liquid
1) Short, open, water	methanol
2) Short, open, methanol	water
3) Short, open, water	30 ppt saline
4) Short, open, 30 ppt saline	water
5) Short, open, methanol	30 ppt saline
6) Short, open, 30 ppt saline	methanol

sensor whose geometry and the equivalent circuit are shown in Fig. 1. The expression for the input admittance seen by the probe aperture when terminated by a medium with the permittivity $\hat{\epsilon}$ is given as [16]:

$$Y(f, \hat{\epsilon}) = Z_o\{G_o(f)\hat{\epsilon}^{5/2} + j\omega C_o(f, \epsilon')\hat{\epsilon} + j\omega C_f(\epsilon')\} \tag{7}$$

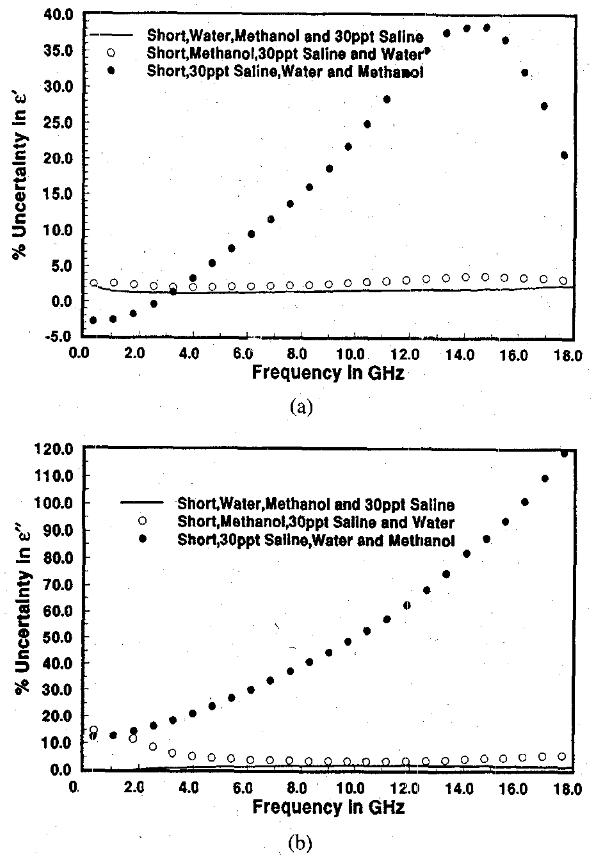
where G_o is the radiation conductance, C_o is the fringing capacitance in the test dielectric, C_f is the fringing capacitance in the coaxial line representing the stored energy due to higher order modes and Z_o is the characteristic impedance of the coaxial line.

The two-port network A, consists of a very short section of the transmission line of a known characteristic admittance and a two-port network P consisting of an admittance (7). In this simulation, a short circuit and two reference liquids are used as calibration standards and a third reference liquid is used as a test liquid. The permittivity of the calibration liquids is computed and perturbed using the uncertainties given in Fig. 2. A simulated calibration is performed based on these perturbed values. The error-correction algorithm is applied to the simulated results for the test liquid. The percentage difference between the resulting and theoretical permittivities of the test material are calculated. This procedure is repeated for various combinations of the reference liquids as calibration standards and the test material. The uncertainties in the error-corrected permittivities of the test liquids due to the uncertainties in the permittivities of the of the reference liquids, are calculated for various combinations of reference and test liquids using probe admittance model of (7). Two important cases are considered in this simulation. In the first case, short ciruict, open circuit and any one of the three reference liquids as the three calibration standards and the remaining two reference liquids are used as the test liquids. In the second case, short circuit, and two of the three reference liquids are used as the three calibration standards and the third reference liquid is used as the test liquid. The results of the calculation are presented in Figs. 3 and 4, respectively.

III. EXPERIMENTS

A. Instrumentation

The measurements were performed using an HP8510B automatic network analyzer (ANA) with the time domain option. The ANA was controlled by an IBM compatible



(a)

(b)

Fig. 4. Relative uncertainties (rms) in the permittivity of test liquid due to the uncertainties in the Cole-Cole parameters of reference liquids used as calibration standards (i = 2, 3) at 26°C. (a) 5 uncertainty in ϵ' and (b) % uncertainty in ϵ''.

Calibration Standards	Test Liquid
1) Short, water, methanol	30 ppt saline
2) Short, methanol, 30 ppt saline	water
3) Short, 30 ppt saline, water	methanol

PC with IEEE-488 interface. All data acquisition software was written in C language. The results of the measurements reported in this paper were obtained with step sweep mode, 200 s dwell time and 256 averages, to ensure sufficient reaction time as well as stable and repeatable measurements. The frequency range used for all these measurements was 0.045 GHz–18.045 GHz with 801 points to ensure high resolution in the time domain. The frequency range and the number of points were selected to utilize the low-pass impulse response option of the ANA for determining a valid short circuit termination.

B. Probe Geometry

The probe used in the experiments was built from a standard 50-Ω teflon-filled 3.6-mm (OD) semirigid coaxial line. The probe was equipped with a SMA connector with the other end machined flat. Using a special tool and a fine sand paper the machined surface was polished such that the end face of the probe was flat and perpendicular to the axis.

C. Permittivity Measurements

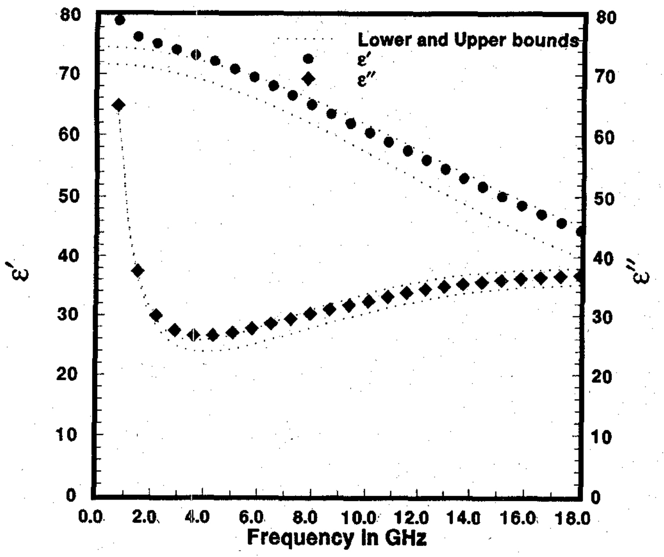


Fig. 5. Permittivity of 15 ppt saline at 26°C along with the uncertainties of measurements resulting from the uncertainties in the Cole–Cole parameters of reference standards.

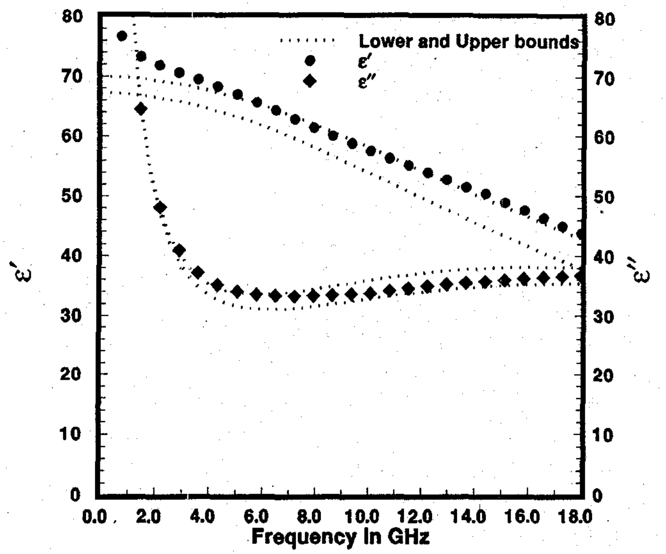


Fig. 6. Permittivity of 30 ppt saline at 26°C along with the uncertainties of measurements resulting from the uncertainties in the Cole–Cole parameters of reference standards.

It is evident from the previous discussion that the measurements of an unknown material can be made accurately by a proper selection of reference liquids as calibration standards. To prove this experimentally, the error-corrected measurements were conducted on saline and methanol at 26°C using short circuit, open circuit and water at 26°C as calibration standards. The expression for admittance of the open-ended coaxial line, given in (7), was used to estimate the aperture admittances of the standards. The permittivity of the reference liquids was estimated based on the equations given in the Appendix A. The resulting permittivities of the test liquids are presented in Figs. 5 and 6 along with the uncertainties of measurements resulting from the uncertainties in the Cole–Cole parameters of the reference liquids.

IV. RESULTS AND DISCUSSIONS

A critical analysis of the permittivity measurements of materials using open-ended sensors is presented. The choice of reference liquids as calibration standards and their effect on the error-corrected permittivity measurements are considered. In general, this analysis is applicable to any open-ended sensor. However, as an example, a 3.6-mm sensor is used here for the presentation of the numerical and experimental data.

It is well known that the accuracy of the error-corrected permittivity measurements of the test material depends on the accuracy with which the calibration standards are known. When the reference liquid is used as a calibration standard, the accurate knowledge of the permittivity of the reference liquid is necessary which requires reliable Cole–Cole parameters data. The variation in the Cole–Cole parameters of various reference liquids is presented in Table I. It is evident that there are considerable differences between the values of the Cole–Cole parameters used by different authors which makes it difficult to compare the results of their permittivity measurements. Hence the uncertainty analysis of the reference liquids was performed. The resulting uncertainties in $\hat{\epsilon}$ due to the uncertainties in the Cole–Cole parameters are shown in Fig. 2. From the relative uncertainty (rms) of the data presented in Fig. 2, it can be seen that the uncertainties in ϵ'' of the reference liquids are larger than the uncertainties in ϵ'. Moreover, at low frequencies, i.e., less than 2.0 GHz, the uncertainties in ϵ'' are quite large. With the exception of methanol, all liquids have less than 4% uncertainty above 2.0 GHz. The data presented in Fig. 2 provide a basis for the prudent selection of the reference liquids as calibration standards.

Based on the uncertainties in the permittivity of the reference liquids, the relative uncertainty in the measured permittivity of the test liquid was estimated for two cases. The first case involved a short circuit, an open circuit and one of the reference liquids as calibration standards. The uncertainties in the permittivity of the test liquids are presented in Fig. 3. Similarly, the second case used a short circuit and two reference liquids as calibration standards. The corresponding uncertainties in the measured permittivity of test liquids are presented in Fig. 4. The above studies are made to examine the sensitivity of the error correction technique to the uncertainties in the calibration standards. From Fig. 3, it can be observed that, when methanol is used as one of the calibration standards, the uncertainties in the measured permittivities of the test liquids are relatively high, of the order of 15%. This can be explained as follows. In general, the three standard error-correction defines a solution domain[1] which is bounded by the three calibration standards. As long as the permittivity of the test material lies within the solution domain, the relative uncertainties of the test material permittivity are relatively small. Using this argument, the relative uncertainties of the test material, for various cases presented in Fig. 3, can be examined. For example, when a short circuit, an open circuit and methanol are used as calibration standards, the uncertainty in the measured permittivity of water is large. Similar behavior can be observed in Fig. 4 for the cases where methanol is used as the test liquid. From the results presented in the Figs. 2, 3, and 4, it is evident that the relative uncertainty in the test liquids due to the uncertainties in the permittivity of the calibration standards is smaller than the uncertainty due to the Cole–Cole parameters. It can be concluded that error correction reduces the relative uncertainty in the permittivity of the reference liquids but does not eliminate the errors introduced by the calibration standards.

Finally, using the open-ended semirigid coaxial sensor and with the error correction, the measurements were performed on 15 and 30 ppt saline. The calibration standards used for these measurements were short circuit, open circuit and water. The measured permittivities are shown in Figs. 5 and 6 along with the measurement uncertainties resulting from the uncertainties in the Cole–Cole parameters of the reference liquids. From Figs. 5 and 6, it can be observed that, for saline solutions, the relative error is of the order of 6% in the real part and less than 2% in the imaginary part in the frequency range 0.045–18 GHz.

V. CONCLUSION

A discussion on the important aspects of the effects of the uncertainties in the permittivity measurements using open-ended sensors due to the uncertainties in the Cole–Cole parameters of the reference liquids is presented. Relative (rms) uncertainties in the permittivities of the reference liquids due to the uncertainties in the Cole–Cole parameters are quantified. The uncertainties in the error-corrected permittivities of the test liquids due to the uncertainties in the permittivities of the reference liquids is estimated. It is observed that the resulting uncertainty in the permittivity of the test material is smaller than the uncertainty in the reference liquid itself. Also, the effect of the choice of reference liquids as calibration standards, on the test liquid permittivities is presented. Water, due to the relatively small uncertainties in its Cole–Cole parameters, represents a better calibration standard than methanol and saline.

APPENDIX A

The tabulated values of the Cole–Cole parameters of reference liquids as a function of temperature are not convenient for use with high-speed digital computers. Hence, simple empirical expressions were derived which are in good agreement with the tabulated values. The expressions for the Cole–Cole parameters for water, methanol and saline were found by fitting the tabulated data using nonlinear regression. The maximum error associated with each of the Cole–Cole parameters was estimated by comparing the tabulated data with the values determined using these expressions.

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[1] The exact pattern of the solution domain is a complex function of the properties of the standards and their materials. This problem is being investigated and will be reported in a separate paper.

A. Cole–Cole Parameters of Water

A(a). Using NBS data [11]: $(0 < T < 60°\mathrm{C})$

$$\epsilon_s = 88.13769 - 3.35924 \times 10^{-1}T - 0.7962 \times 10^{-2}T^2 + 0.288 \times 10^{-3}T^3 + 0.0273 \times 10^{-4}T^4 \pm 0.326 \tag{A1.1}$$

$$\epsilon_\infty = 4.991979 + 0.0801 \times 10^{-1}T - 0.0609 \times 10^{-2}T^2 + 0.0326 \times 10^{-3}T^3 + 0.00341 \times 10^{-4}T^4 \pm 0.088 \tag{A1.2}$$

$$\lambda_s = 0.489491 + 2.8616111e^{-0.0399892T} \pm 0.033 \text{ cm} \tag{A1.3}$$

$$\tau = \frac{\lambda}{2\pi c}\, s \tag{A1.4}$$

$$\alpha = 0. \tag{A1.5}$$

A(b). Cole–Cole Parameters of Water Used by the Authors: $0 < T < 100°\mathrm{C}$)

The expression for static permittivity ϵ_s [12] is given by

$$\epsilon_s = 87.74 - 4.0008 \times 10^{-1}T + 0.09398 \times 10^{-2}T^2 - 0.00141 \times 10^{-3}T^3 \pm 0.009. \tag{A2.1}$$

From [13], the optical permittivity ϵ_∞ is given as

$$\epsilon_\infty = 4.5 \tag{A2.2}$$

The tabulated data [13] of the critical wavelengths as a function of temperature is used to find the expression for the relaxation time.

$$\tau = 17.68703 - 6.2240692 \times 10^{-1}T + 1.263 \times 10^{-2}T^2 - 0.1354 \times 10^{-3}T^3 + 0.005631 \times 10^{-4}T^4 \pm 0.0372 \text{ ps} \tag{A2.3}$$

and the distribution parameter α is given by [13]

$$\alpha = 0.02. \tag{A2.4}$$

B. Cole–Cole Parameters of Methanol

B(a). Using NBS Data [11]: $(0 < T < 50°\mathrm{C})$

$$\epsilon_s = 37.98145 - 2.32834 \times 10^{-1}T + 0.0816 \times 10^{-2}T^2 - 0.00406 \times 10^{-3}T^3 + 0.000228 \times 10^{-4}T^4 \pm 0.042 \tag{A3.1}$$

$$\epsilon_\infty = 6.10102 - 0.21889 \times 10^{-1}T + 0.00823 \times 10^{-2}T^2 - 0.001325 \times 10^{-3}T^3 + 0.00000996 \times 10^{-4}T^4 \pm 0.047 \tag{A3.2}$$

$$\lambda_s = 15.9995 - 3.865188 \times 10^{-1}T + 0.5076 \times 10^{-2}T^2 - 0.04213 \times 10^{-3}T^3 + 0.0022083 \times 10^{-4}T^4 \pm 0.004 \text{ cm} \tag{A3.3}$$

$$\tau = \frac{\lambda_s}{2\pi c}\, s \tag{A3.4}$$

$$\alpha = 0 \tag{A3.5}$$

B(b). Cole–Cole Parameters of Methanol Used by the Authors: $(0 < T < 40°\mathrm{C})$

These expressions are found by using the tabulated data [18]:

$$\epsilon_s = 39.2 - 0.22T \tag{A4.1}$$

$$\epsilon_\infty = 4.95 - 0.024T \pm 0.17 \tag{A4.2}$$

$$\tau = 86.94091 - 18.13167 \times 10^{-1}T + 1.285 \times 10^{-2}T^2 \pm 0.182 \text{ ps} \tag{A4.3}$$

$$\alpha = 0.0168809 + 1.000129T^{1.418277} - 0.998363T^{1.418743} \pm 0.001 \tag{A4.4}$$

C. Cole–Cole Parameters of Saline Used by the Authors: $(0 < T < 40°\mathrm{C})$

The expressions for the static permittivity and the relaxation time of water are used to fit the Cole–Cole parameter data [20], in conjunction with the expressions [15]:

$$\epsilon_s(T, 0) = 87.74 - 4.0008 \times 10^{-1}T + 0.09398 \times 10^{-2}T^2 - 0.00141 \times 10^{-3}T^3 \pm 0.009 \tag{A5.1}$$

From [13], the optical permittivity ϵ_∞ is given as

$$\epsilon_\infty = 4.5 \tag{A5.2}$$

$$\tau(T, 0) = 17.68703 - 6.2240692 \times 10^{-1}T + 1.263 \times 10^{-2}T^2 - 0.1354 \times 10^{-3}T^3 + 0.005631 \times 10^{-4}T^4 \pm 0.0372 \text{ ps} \tag{A5.3}$$

$$\alpha = 0.02 \tag{A5.4}$$

$$\epsilon_s(T, N) = \epsilon_s(T, 0)a(N) \pm 1.052 \tag{A5.5}$$

$$\tau(T, N) = \tau(T, 0)b(N, T) \pm 1.013 \text{ ps} \tag{A5.6}$$

where $a(N)$ and $b(N, T)$ are functions temperature and normality N. They are given by [15] as

$$a(N) = 1.00 - 0.2551N + 5.151 \times 10^{-2}N^2 - 6.889 \times 10^{-3}N^3 \tag{A5.7}$$

$$b(N, T) = 0.1463 \times 10^{-2}NT + 1.0 - 0.04896N - 2.967 \times 10^{-2}N^2 + 5.644 \times 10^{-3}N^3 \tag{A5.8}$$

Since the salt content in water is often described in terms of the salinity, S, it is convenient to have a relation between the normality and salinity. This is given by

$$N = S(1.707 \times 10^{-2} + 1.205 \times 10^{-5}S + 4.058 \times 10^{-9}S^2). \tag{A5.9}$$

Finally, the ionic conductivity σ of saline as a function of temperature and normality is expressed as

$$\begin{aligned}\sigma(T, N) = \sigma(25, N)(1.0 &- 1.962 \times 10^{-2}\,\Delta + 8.08 \\ &\times 10^{-5}\,\Delta^2 - \Delta N(3.020 \times 10^{-5} \\ &+ 3.922 \times 10^{-5}\,\Delta + N(1.721 \times 10^{-5} \\ &- 6.584 \times 10^{-6}\,\Delta))) \qquad \text{(A5.10)}\end{aligned}$$

and

$$\begin{aligned}\sigma(25, N) = N(10.394 &- 2.3776N + 0.68258N^2 \\ &- 0.13538N^3 + 1.0086 \times 10^{-2}N^4) \qquad \text{(A5.11)}\end{aligned}$$

where $\Delta = 25 - T$.

Appendix B

The general dispersion equation for the permittivity is

$$\hat{\epsilon} = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} - j\frac{\sigma}{\omega\epsilon_o}. \qquad \text{(B1.1)}$$

The locus of $\hat{\epsilon}$ in the complex plane is a segment of a semicircle with the parametric representation:

$$\epsilon' = \frac{(\epsilon_s - \epsilon_\infty)}{2}\left\{1 - \frac{\sinh\left[(1-\alpha)\ln\omega\tau\right]}{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}}\right\} + \epsilon_\infty \qquad \text{(B1.2)}$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)}{2}\left\{\frac{\cos\alpha\frac{\pi}{2}}{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}}\right\} + \frac{\sigma}{\omega\epsilon_o} \qquad \text{(B1.3)}$$

The uncertainties (rms) in the real and imaginary parts of the permittivity due to the uncertainties in the Cole–Cole parameters can be expressed as

$$\Delta\epsilon' = \sqrt{\left\{\left(\frac{\partial\epsilon'}{\partial\epsilon_s}\Delta\epsilon_s\right)^2 + \left(\frac{\partial\epsilon'}{\partial\epsilon_\infty}\Delta\epsilon_\infty\right)^2 + \left(\frac{\partial\epsilon'}{\partial\alpha}\Delta\alpha\right)^2 + \left(\frac{\partial\epsilon'}{\partial\tau}\Delta\tau\right)^2\right\}} \qquad \text{(B1.4)}$$

$$\Delta\epsilon'' = \sqrt{\left\{\left(\frac{\partial\epsilon''}{\partial\epsilon_s}\Delta\epsilon_s\right)^2 + \left(\frac{\partial\epsilon''}{\pi\epsilon_\infty}\Delta\epsilon_\infty\right)^2 + \left(\frac{\partial\epsilon''}{\partial\alpha}\Delta\alpha\right)^2 + \left(\frac{\partial\epsilon''}{\partial\tau}\Delta\tau\right)^2 - \left(\frac{\partial\epsilon''}{\partial\sigma}\Delta\sigma\right)^2\right\}} \qquad \text{(B1.5)}$$

where Δ's are the uncertainties in the Cole–Cole parameters. The partial derivatives of the real and the imaginary parts of the permittivity with respect to the Cole–Cole parameters can be derived from (B1.2) and (B1.3). They are given below for easy reference:

$$\frac{\partial\epsilon'}{\partial\epsilon_s} = \frac{1}{2}\left\{1 - \frac{\sinh\left[(1-\alpha)\,n\omega\tau\right]}{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}}\right\} \qquad \text{(B1.6)}$$

$$\frac{\partial\epsilon'}{\partial\epsilon_\infty} = \left\{1 - \frac{\partial\epsilon'}{\partial\epsilon_s}\right\} \qquad \text{(B1.7)}$$

$$\frac{\partial\epsilon'}{\partial\alpha} = \frac{(\epsilon_s - \epsilon_\infty)}{2}\left\{\frac{\ln\omega\tau\left\{1 + \sin\alpha\frac{\pi}{2}\cosh\left[(1-\alpha)\ln\omega\tau\right]\right\} + \frac{\pi}{2}\cos\alpha\frac{\pi}{2}\sinh\left[(1-\alpha)\ln\omega\tau\right]}{\left\{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}\right\}^2}\right\} \qquad \text{(B1.8)}$$

$$\frac{\partial\epsilon'}{\partial\tau} = -\frac{(\epsilon_s - \epsilon_\infty)}{2}\frac{(1-\alpha)}{\tau}\left\{\frac{1 + \sin\alpha\frac{\pi}{2}\cosh\left[(1-\alpha)\ln\omega\tau\right]}{\left\{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}\right\}^2}\right\} \qquad \text{(B1.9)}$$

$$\frac{\partial\epsilon''}{\partial\epsilon_s} = \frac{1}{2}\left\{\frac{\cos\alpha\frac{\pi}{2}}{\cosh\left[(1-\alpha)\ln\omega\tau\right] + \sin\alpha\frac{\pi}{2}}\right\} \qquad \text{(B1.10)}$$

$$\frac{\partial\epsilon''}{\partial\epsilon_\infty} = -\frac{\partial\epsilon''}{\partial\epsilon_s} \qquad \text{(B1.11)}$$

$$\frac{\partial \epsilon''}{\partial \alpha} = \frac{(\epsilon_s - \epsilon_\infty)}{2} \left\{ \frac{\ln \omega\tau \cos \alpha \frac{\pi}{2} \sinh [(1 - \alpha) \ln \omega\tau] - \frac{\pi}{2} \left\{ 1 + \sin \alpha \frac{\pi}{2} \cosh [(1 - \alpha) \ln \omega\tau] \right\}}{\left\{ \cosh [(1 - \alpha) \ln \omega\tau] + \sin \alpha \frac{\pi}{2} \right\}^2} \right\} \tag{B1.12}$$

$$\frac{\partial \epsilon''}{\partial \tau} = -\frac{(\epsilon_s - \epsilon_\infty)}{2} \frac{(1 - \alpha)}{\tau} \left\{ \frac{\cos \alpha \frac{\pi}{2} \sinh [(1 - \alpha) \ln \omega\tau]}{\left\{ \cosh [(1 - \alpha) \ln \omega\tau] + \sin \alpha \frac{\pi}{2} \right\}^2} \right\} \tag{B1.13}$$

$$\frac{\partial \epsilon''}{\partial \sigma} = \frac{1}{\omega \epsilon_o} \tag{B1.14}$$

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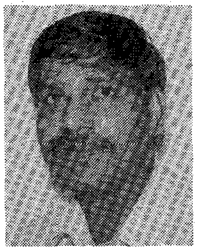

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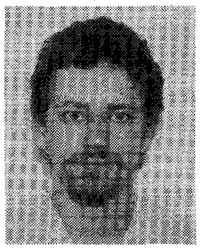

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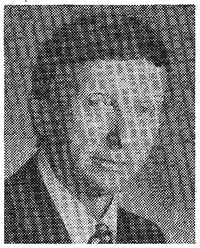

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