# A Dielectric Spectrometer for Liquid Using the Electromagnetic Induction Method

Key parameters of colloids are often directly related to or can be derived from permittivity or conductivity. Dielectric dispersion analysis (dielectric spectroscopy) yields insights into colloidal properties. A dielectric meter using a new sensing technique has been developed.

by Hideki Wakamatsu

Dielectric spectroscopy is useful for the characterization of colloidal dispersions. In the past, dielectric spectroscopy has been attempted using parallel metal electrodes to measure the permittivity and conductivity of colloids. However, it is difficult in practice to make these measurements in conductive solutions because large measurement errors can be caused by electrode polarization, which is a kind of contact impedance between the electrode and the solution. Electrode polarization behaves like a capacitance and masks the true properties of the solution at low frequencies.

The HP E5050A colloid dielectric probe was developed for colloidal liquid evaluation. Its electromagnetic induction technique eliminates the electrode polarization effect. The probe operates from 75 kHz to 30 MHz with the HP 4285A precision LCR meter and HP VEE software on an HP Vectra or compatible computer (Fig. 1). The HP VEE environment[1] provides easy operation, display, and analysis of the measurement data.
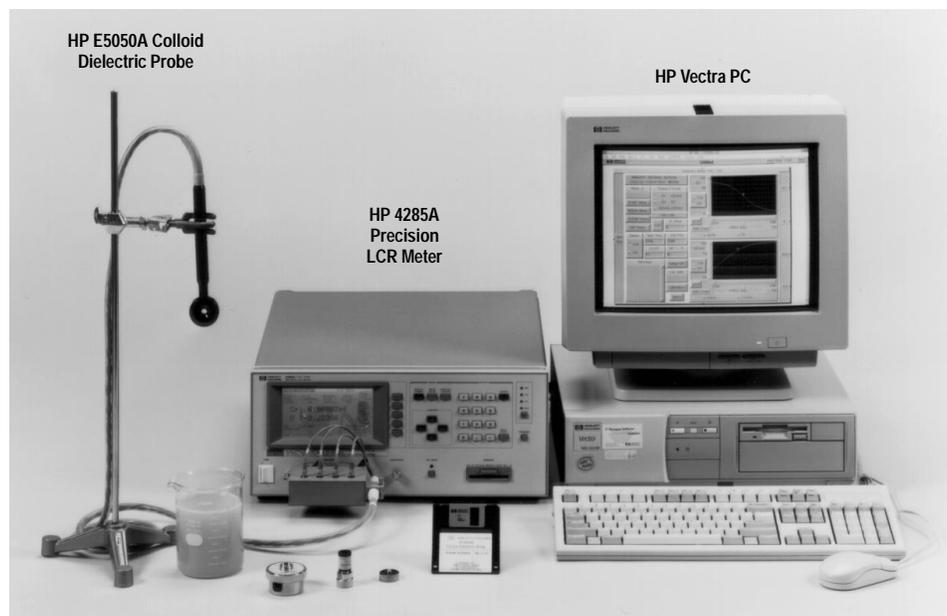
Fig. 1. *HP E5050A colloid dielectric probe and system.*

Background of Dielectric Spectroscopy

Colloids are dispersion systems composed of a dispersed substance in particulate form in a continuous-phase dispersion medium. There are many types of colloid; some familiar examples are listed in Table I.

Table I
Familiar Colloids

Colloid	Dispersion Medium	Dispersed Substance
Shaving Foam	Soapy Water (liquid)	Air, Propane (gas)
Fog, Cloud	Air (gas)	Water (liquid)
Milk, Mayonnaise	Water (liquid)	Fat, Oil (liquid)
Butter, Margarine	Fat, Oil (liquid)	Water (liquid)
Charcoal	Carbon (solid)	Air (gas)
Blood	Serum (liquid)	Erythrocyte (microcapsule)
Black Ink	Water (liquid)	Carbon Black (solid)

Since there are interfaces between the dispersed substance and the surrounding dispersion medium in a colloidal dispersion, there can be appended (nonintrinsic) dielectric relaxations—typically the permittivity decreases and the conductivity increases with increasing frequency—as a result of interfacial polarization caused by charge buildup on the boundaries between the different materials. The analysis of these dielectric relaxations based on an appropriate theory of interfacial polarization provides valuable information on the structural and electrical properties of colloidal particles.[2]

The frequency characteristics of the permittivity and conductivity of colloidal solutions are especially informative. Fig. 2 shows some examples. A practical means of measuring these characteristics—that is, practical dielectric spectroscopy— would be a significant contribution to the study of the stabilization of dispersion systems and product quality control.

Dielectric Measurement of Colloidal Solutions

Traditionally, permittivity is measured with parallel metal electrodes. This technique can be used to measure nonconducting (nonionic) solutions such as oils or alcohols. However, in the case of salty or ionic solutions that have high conductivity, this method suffers from large measurement errors. Fig. 3a shows the mechanism responsible for the errors. Electrode polarization results from the electrical double layer between the metal electrode surface and the ionic solution. This becomes a serious problem at low frequencies because electrode polarization is a capacitance, so the contact impedance is large at low frequencies. If the total impedance consisting of the solution impedance and the electrode polarization impedance is counted as the solution impedance, a large error is incurred at low frequencies (Fig. 3b). In other words, the increase of the contact impedance at low frequencies masks the true properties of the solution.

The second reason why it is difficult to make permittivity measurements is as follows. Often in aqueous colloid spectroscopy, the permittivity is a minor part of the admittance compared to the conductivity. This means that it takes a highly precise measurement to extract the small capacitive permittivity component from the almost entirely conductive admittance. For example, in 0.1% aqueous NaCl ($\varepsilon_r = 80$, $\kappa = 0.2$ S/m), the magnitude of the susceptance (the permittivity part) is only about 1/500 that of the conductance (the conductivity part) at 100 kHz. If 1% accuracy of the permittivity analysis is required, the measurement system must measure the argument of the complex admittance accurately within 20 microradians.

Nonelectrode Electromagnetic Induction Method

If the electrode polarization could be removed, the true impedance of the solution could be measured. To eliminate the electrode polarization, a measurement technique without electrodes has been implemented. In this method, a closed-circuit current is made to flow in the solution by electromagnetic induction. This current is then measured, also by electromagnetic induction.

Fig. 4 illustrates the principle of this measurement technique. When a pair of toroidal coils are immersed in the solution, the solution completes the circuit between the coils. When the primary coil is excited from the ac signal source, a magnetic field in the primary coil induces an electric field around the primary and secondary coils, and the electric field causes a closed-circuit current in the solution. This closed circuit current induces a magnetic flux in the secondary coil and the magnetic flux induces an electromotive force in the secondary coil. If the current flowing in the secondary coil is measured, the current in the solution can be determined. Since the magnitudes of the currents in the solution and the secondary coil are proportional to the closed-circuit solution admittance, the conductivity or permittivity of the solution can be calculated from the measured secondary current and primary voltage.

The induction method avoids the electrode polarization effect and has been used in some conductivity meters suited for high-conductivity solutions. However, while these meters can measure conductivity, they cannot measure permittivity because of the difficulty of measuring the small capacitive part of the admittance, as discussed in the last section. The capacitive part (i.e., permittivity) of the admittance is much smaller than the conductive part for most aqueous solutions.
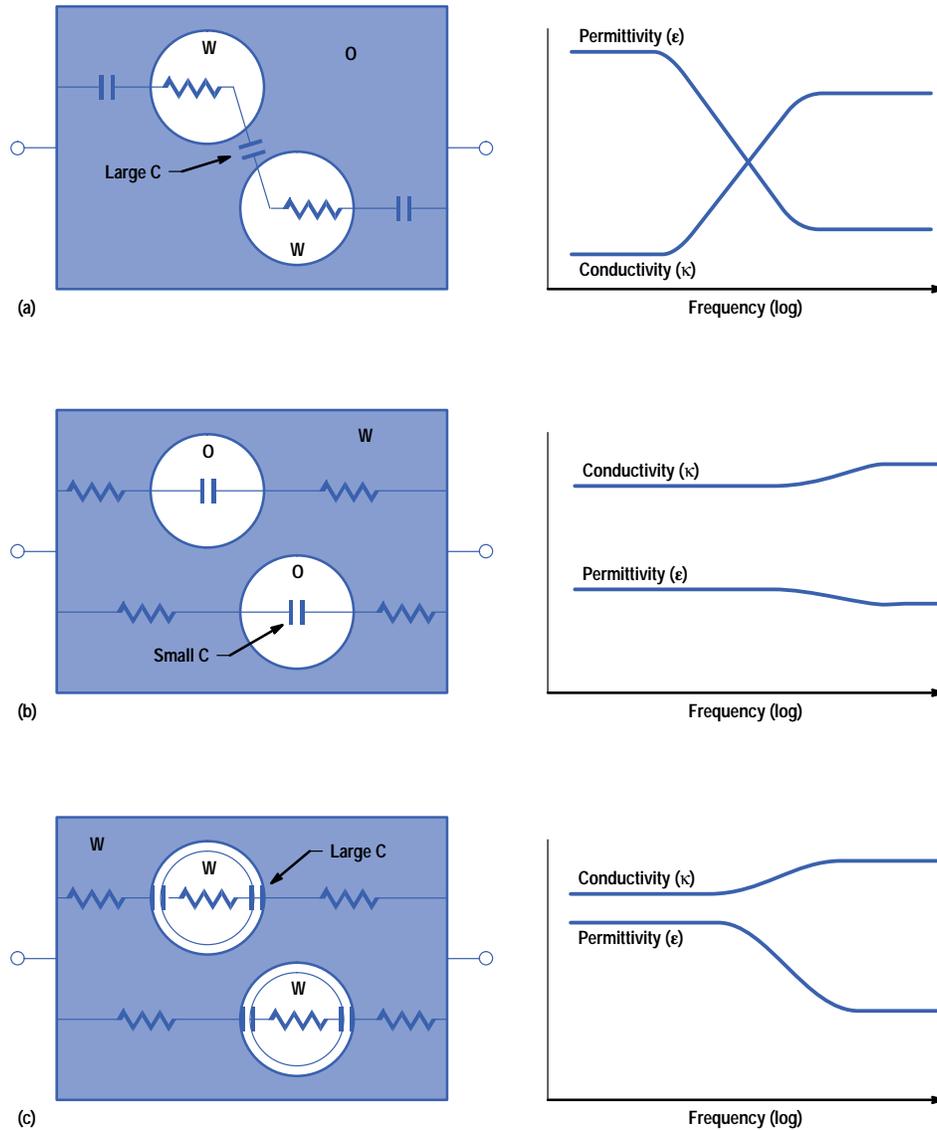
Fig. 2. *Appended dielectric relaxations: mechanisms (left) and frequency characteristics (right). (a) Water-in-oil emulsion. (b) Oil-in-water emulsion. (c) Microcapsule-in-water suspension.*
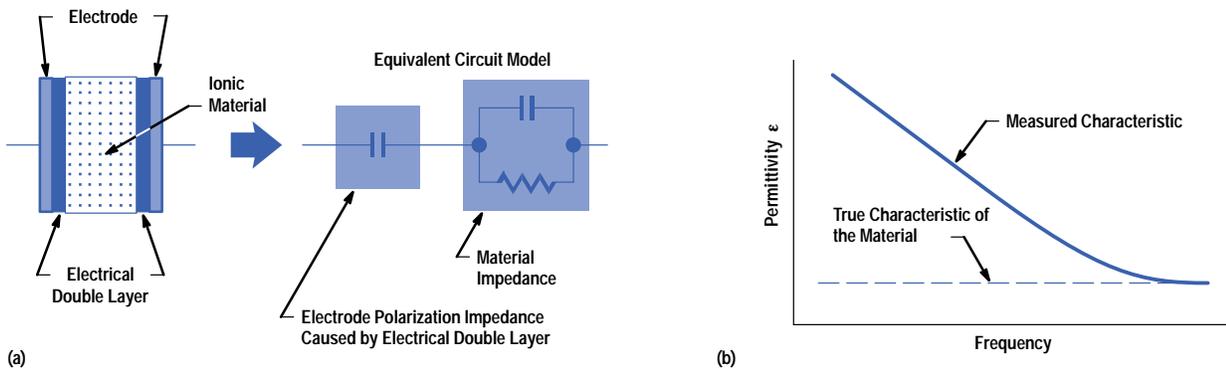
**Fig. 3.** *Electrode polarization effect. (a) Mechanism. (b) Effect on measured frequency characteristic.*

When a detection device such as shown in Fig. 4 is used to measure a capacitance, measurement errors are produced by undesired coupling between the primary and the secondary. This coupling includes leakage magnetic flux coupling, stray capacitance coupling, and acoustic coupling caused by magnetic distortion of the magnetic cores. All of these are severe problems even if the amount of coupling is small because the secondary current corresponding to the permittivity is

extremely small, even for liquid that has a relatively large permittivity, such as water. This current is often less than one millionth of the primary current at low frequencies (e.g., < 100 kHz).
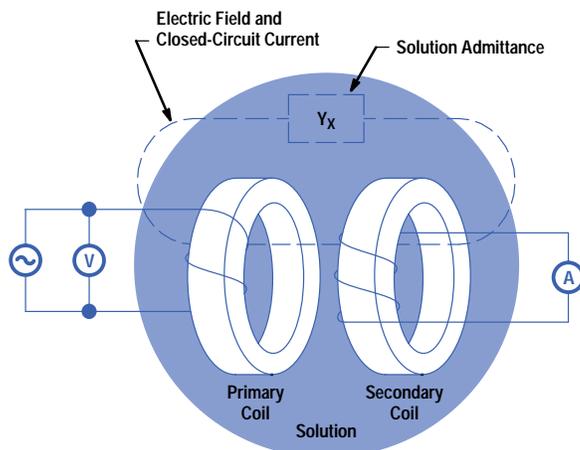
Fig. 4. *Electromagnetic induction method.*

We have developed a new probe and system to solve the problems discussed above. As mentioned earlier, the probe operates from 75 kHz to 30 MHz with the HP 4285A precision LCR meter and HP VEE software on an HP Vectra or compatible computer. The HP 4285A applies 1V to the primary coil, achieves accuracy on the order of 50 microradians or 200 picoamperes in the secondary coil current measurement, and then outputs the vector ratio of the current to the primary voltage, which is measured remotely (Fig. 5). The permittivity and conductivity, which are functions of the vector ratio, are calculated from the measured vector ratio by the software in the computer.
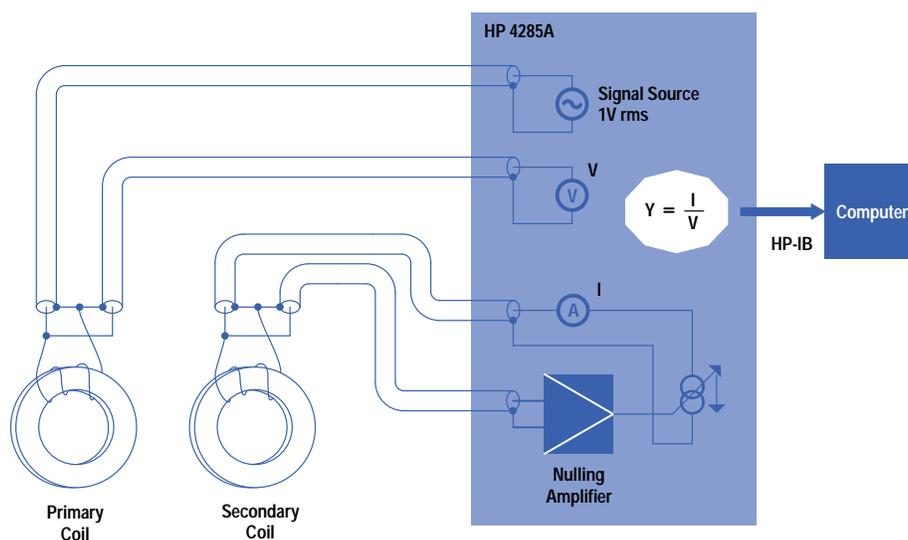

Fig. 5. *Simplified schematic diagram of the probe and LCR meter.*

Probe Architecture

The induction method completely eliminates electrode polarization. However, some improvements to reduce the undesired couplings were necessary for practical use.

The first prototype of the probe had the structure shown in Fig. 6. The interior of this probe consists of two toroidal coils and electrostatic shields, which are covered with epoxy resins. This prototype yielded knowledge in three key areas.

First, although extremely delicate, permittivity measurement is possible. In spite of the tight shield between the primary and secondary coils, the residual admittance from the undesired couplings can be larger than the effective admittance from the permittivity of water (Fig. 7). However, this residual admittance can be canceled out with the assistance of software corrections.
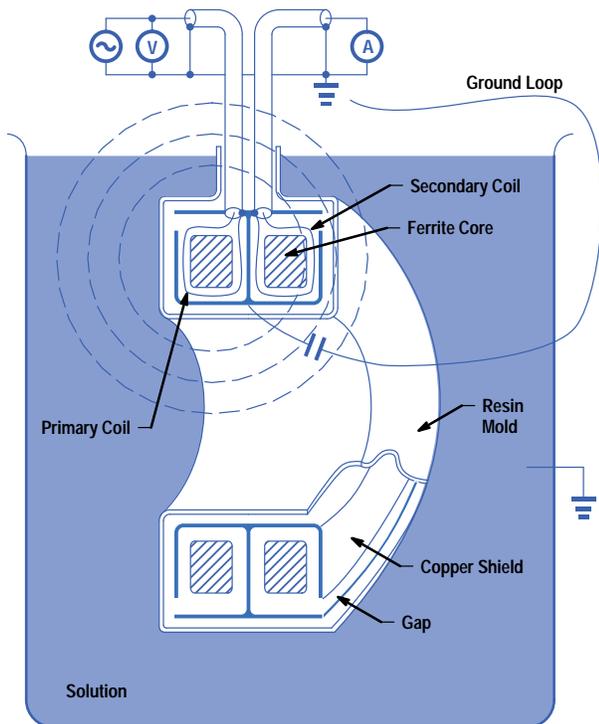
Fig. 6. *Structure of the first prototype probe.*
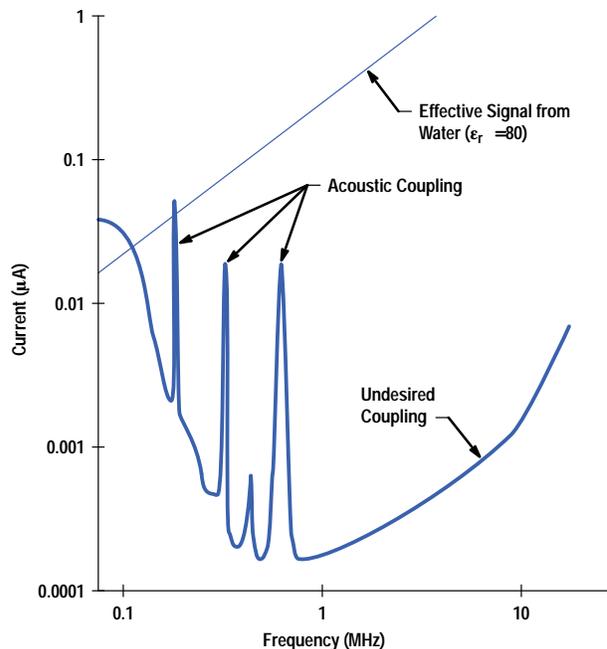
Fig. 7. *Effect of coupling on secondary coil current in water.*

Second, an asymmetrical electric field produces an error if there is a ground loop. When measuring solutions on a beaker scale, where the solution is not grounded, there is no problem using the structure shown in Fig. 6. However, if the solution container is on a tank scale and the solution is nearly grounded, a new problem arises. The asymmetrical field such as the one shown in Fig. 6 produces unbalanced voltages on the symmetrical shield structure. This common-mode voltage produces a ground-loop current, which is measured like an offset capacitance (permittivity). This offset phenomenon is very critical because it is unstable and often larger than the permittivity of water. To eliminate this offset effect, the probe structure must generate a balanced field.

Third, acoustic (microphonic) coupling also produces severe problems. The shape of a ferrite core that has a large permeability is geometrically transformed by a magnetic field. Vibration of the magnetized core produces an electromotive force in the coil wound on the core. When the primary coil is excited from the ac signal source, the primary core vibrates. The secondary core picks up this mechanical vibration and produces an electromotive force in the secondary coil if the secondary core is magnetized. This mechanism spoils the isolation between the primary and the secondary. Since the toroidal cores have many resonant modes of mechanical vibration between 100 kHz and 1 MHz, they produce sharp peaks of residual admittance at specific frequencies (Fig. 7). This residual admittance cannot be canceled out by corrections because it is unstable: its magnitude and frequency depend on the temperature, the magnetization state, and other factors. To prevent this coupling, a suitable buffer material is required between the primary and secondary cores.

On the basis of the above knowledge, a new probe structure was developed. Fig. 8 shows the final structure.

Accuracy Enhancement: Calibration and Compensation

Permittivity measurement is extremely delicate. Corrections are very important to extract the small capacitive component from the almost entirely conductive admittance and to cancel out the residual admittance of the probe.

Open/Short/Load (OSL) Calibration. The equivalent circuit of the probe with the LCR meter is shown in Fig. 9. The solution's loop admittance Y_x and the LCR meter's measurement value Y_m are related by the following equation based on general impedance measurement theory:

$$Y_x = K_1 \frac{K_2 + Y_m}{1 + K_3 Y_m}, \qquad (1)$$

where K_1, K_2, and K_3 are frequency dependent complex constants. The K_1, K_2, and K_3 are parameters related to the circuit of the measurement system and can be derived from the circuit constants. However, it is not necessary to analyze the details of the circuit. The best way to determine K_1, K_2, and K_3 is known as open/short/load (OSL) calibration. The three unknown parameters can be calculated from the relationship between the values (Y_x) of three known admittances and their measured values (Y_m).
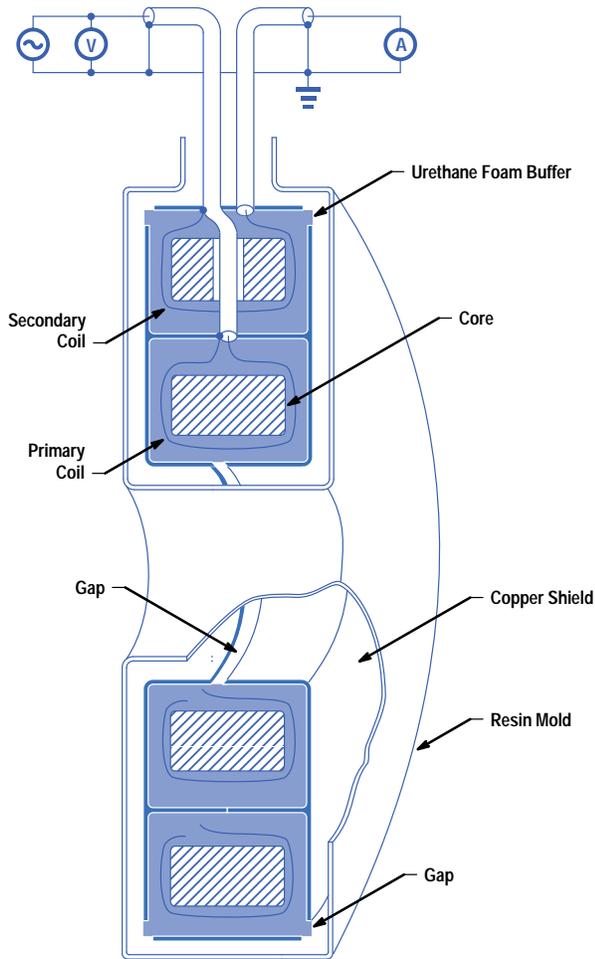
**Fig. 8.** *Final probe structure.*
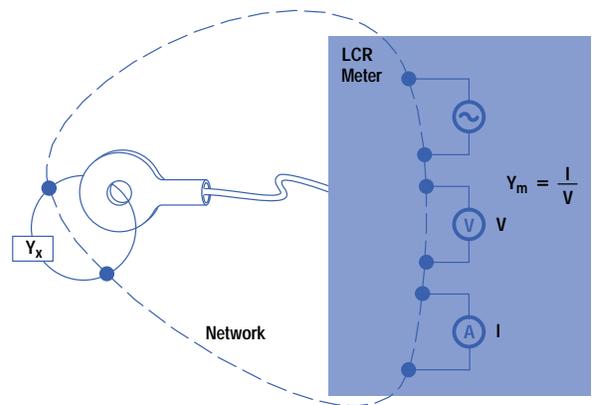
Fig. 9. *Calibration model for probe with LCR meter.*

The three known admittances can be prepared solutions, but a simpler, more accurate, and more stable calibration method is used in our system. The calibration kit shown in Fig. 10 was developed for the OSL calibration of the probe. The kit consists of 50-ohm and 0-ohm one-port standards and an adapter that links the standards with the probe ring. For the load state the probe is placed in the adapter connected to the 50-ohm standard, for the short state the probe is placed in the adapter connected to the 0-ohm standard, and for the open state the probe is placed in air.
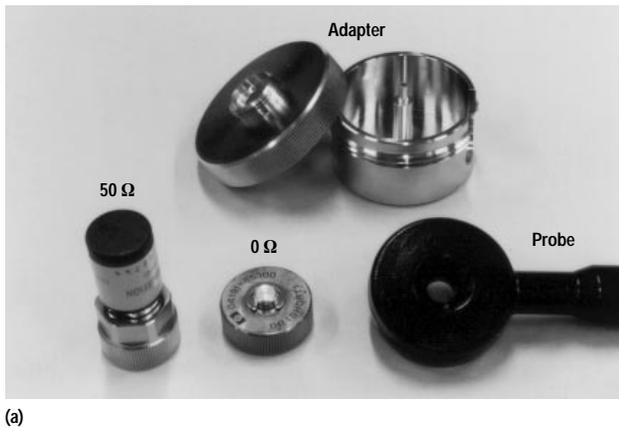
(a)
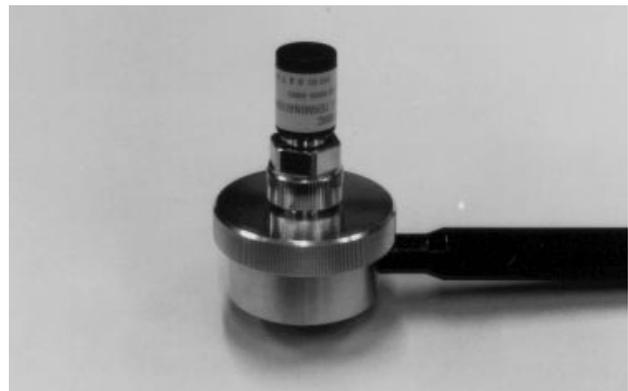
(b)

Fig. 10. *Calibration kit.*

When measuring a solution under test the following relationships exist between the admittance Y_x and the conductivity and permittivity.

$$\text{Conductivity: } \kappa = K_{cell}\text{Re}(Y_x) \quad [\text{S/m}] \tag{2}$$

$$\text{Permittivity: } \varepsilon = K_{cell}\text{Im}(Y_x)/\omega \quad [\text{F/m}] \tag{3}$$

Relative permittivity: $\varepsilon_r = \varepsilon/\varepsilon_o$, $\varepsilon_o = 8.85 \times 10^{-12}$ F/m.

K_{cell} [m^{-1}] is a frequency independent, real-number constant related to the probe dimensions. Re(Y_x) and Im(Y_x) are the real and imaginary parts of Y_x, and ω is angular frequency. Measurement of a known solution (e.g., KCl in water) can determine the K_{cell} value, which needs to be obtained only once in the developmental stage of the probe. This is because the probe is molded, and the probe-to-probe variations in its dimensions are insignificant. Differences in the dimensions of the probe do produce errors in the amplitudes of the measured values, but the value of primary importance for measuring permittivity in conductive solutions is the argument of the complex admittance rather than the amplitude.

Compensation. In theory the OSL calibration should provide all the correction that is necessary. However, a problem was discovered when the conductivity and permittivity of a standard KCl solution were measured after calibration. The K_{cell} derived from the real part (conductivity part) of Y_x and another K_{cell} derived from the imaginary part (permittivity part) of Y_x did not coincide. In other words, while the K_{cell} value should be determined uniquely by the probe shape, in practice a K_{cell} value determined this way will give the wrong answer for either conductivity or permittivity. For example, when using the K_{cell} value determined for conductivity, the calculated permittivity of conductive water was usually 30% to 50% smaller than its true value. Furthermore, this error varies depending on the conductivity, permittivity, and measurement frequency. To solve this problem, the error model shown in Fig. 11 was developed.
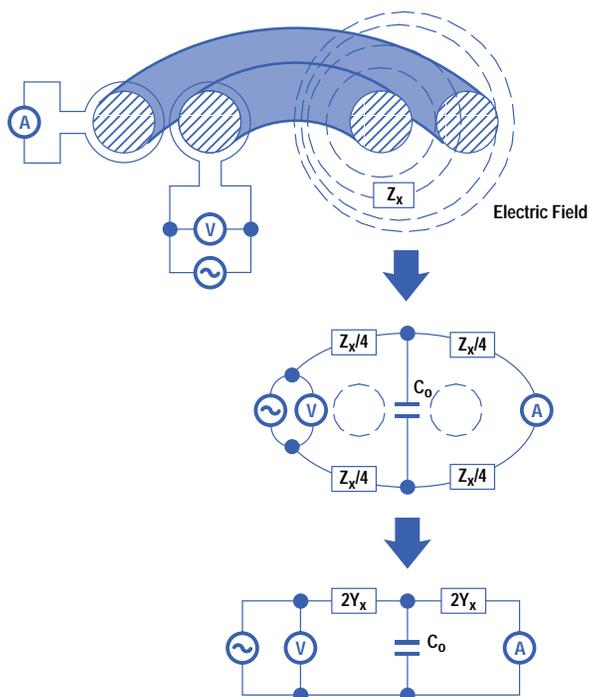

Fig. 11. *Error model involving stray capacitance C_o.*

The compensation equation derived from the model in Fig. 11 is:

$$Y_{x\text{-true}} = \frac{1 + \sqrt{1 + Y_o/Y_x}}{2}Y_x, \tag{4}$$

where $Y_{x\text{-true}}$ is the compensated Y_x, $Y_o = j\omega C_o$, and C_o is a characteristic stray capacitance between the copper shield in the probe mold and the surrounding solution. By using $Y_{x\text{-true}}$ instead of Y_x in equation 2 or 3, the inconsistency between the K_{cell} values for conductivity and permittivity can be improved from 50% to less than 2%. Fig. 12 illustrates the efficacy of the compensation in permittivity.

The value of C_o is determined easily after determining the K_{cell} for conductivity. A solution with a known permittivity (e.g., water: $\varepsilon_r = 80$) is measured, and a C_o value is found that gives the correct permittivity when used in equations 3 and 4.
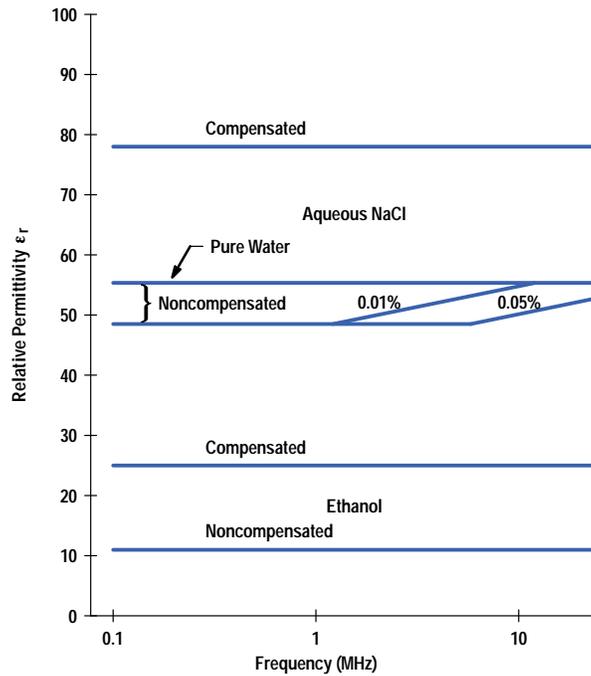
Fig. 12. *Effect of compensation on measured permittivity. (The true values of ε_r at 25°C are 78.3 for water and 24.6 for ethanol.)*

This method would not work if the conductivity and permittivity were to interact, since K_{cell} and C_o would then be difficult to determine independently. However, the effect of C_o on the measured conductivity value is insignificant.

Applications

There are many researchers using dielectric spectroscopy to evaluate colloids. Examples include water-in-oil and oil-in-water emulsions, microcapsule suspensions, biomass monitoring in fermentation, and liposomes. The relations between colloidal structures and dielectric relaxations can be expressed as equations. By measuring the dielectric properties, the researchers hope to measure the structure, geometry, and dimensions of dispersed substances in detail and quantitatively. We expect that the HP E5050 probe will help make such research practical and efficient by eliminating electrode polarization. We will demonstrate two examples of its application.

The first example is liquid car wax. Wax is a water-in-oil colloid that has dielectric relaxation characteristics. Fig. 13 shows the relative permittivity and conductivity for six samples of wax. The samples can be classified into three types of colloidal structures based on their relaxation curves. Noisy data was obtained for low conductivities. It might be more suitable to use
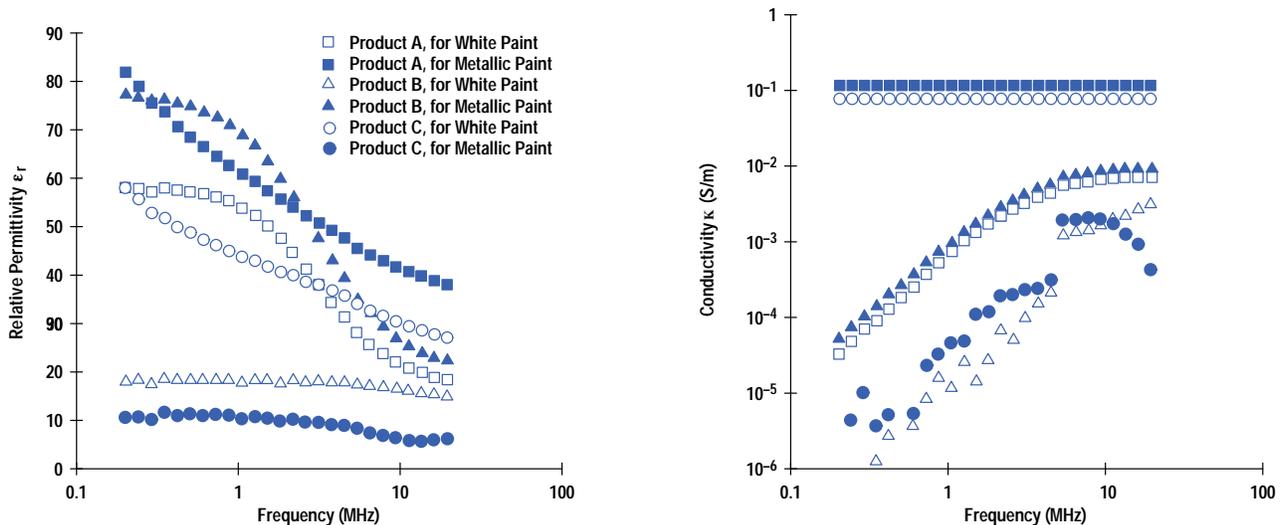
Fig. 13. *Dielectric relaxation of six liquid car waxes.*

the metal electrode method for low conductivities and low permittivities, but the induction method should be used for high conductivities.

The second demonstration is monitoring yeast growth in fermentation. Dielectric spectroscopy is a noninvasive technique suitable for characterizing living biological cells. Biological cells are enveloped in a plasma membrane that is 5 to 10 nm thick. The conductivity of the plasma membrane of a viable cell is negligibly small compared with that of the external medium and the cytoplasm. Since the medium-membrane-cytoplasm structure has the structure of a dielectric material sandwiched between two electrodes, it behaves like a capacitor, and the permittivity of a medium containing cells is larger than that of an empty medium. The increase in the permittivity is proportional to the cell concentration (Fig. 14). Thus, the cell concentration in the cell culture can be monitored by the dielectric method.
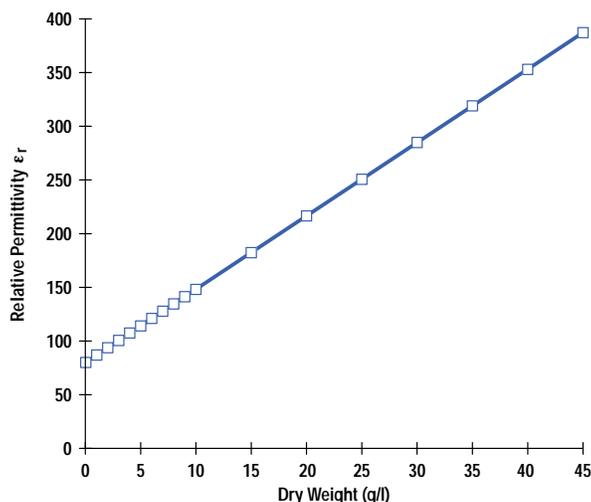
Fig. 14. *Relative permittivity (at 300 kHz) as a function of yeast concentration in fermenting beer.*

Advantages of the HP E5050A system for this application are as follows:

- The technique is nondestructive and requires no sample preparation before analysis. The measurement is quick and simple and online monitoring can be easily realized with computer control.
- Fermentations use ionic culture media, that is, high-conductivity aqueous solutions. The induction probe can eliminate the electrode polarization problem and can measure the permittivity with the required accuracy.
- The dielectric method counts only viable cells. Dead cells with plasma membranes that are leaky to ions are not polarized and are not counted. The method is insensitive to turbid and colored culture media and carbon dioxide bubbles.

Fig. 15 shows the relative permittivity change in beer fermentation at 12°C. The dielectric online monitoring of beer fermentation has succeeded only when the electrodeless method was used. The measurements were made at frequencies between 0.1 MHz and 3.1 MHz. The increase in permittivity up to 80 hours is because of the increase in cell concentration and the increase in cell volume. The undulating curves at low frequencies found at the early stage of the fermentation are caused by highly synchronized yeast growth.[3] The data can reveal not only the cell concentration but also information about cell shape, the plasma, and the membrane that is useful to chemists and biologists.

Summary

Quantitative information about the structure of colloidal dispersions can be obtained from the frequency characteristics of their dielectric properties. The practical realization of dielectric spectroscopy represents a major contribution to the study of the stabilization of dispersion systems and product quality control. Because it is nondestructive, dielectric spectroscopy is also suitable for characterizing living biological cells.

Traditionally, permittivity or conductivity measurements have been made with parallel metal electrodes. However, for conductive colloids, it is difficult to get enough measurement accuracy in practice because this method has large measurement errors caused by electrode polarization.

Electrode polarization can be eliminated by using an induction method, but permittivity measurement is still extremely delicate. In many situations of aqueous colloid spectroscopy, the permittivity is a minor part of the admittance in comparison with the conductivity, so precise measurements are required. We have developed a suitable probe structure and some correction methods for aqueous colloids. The structure realizes the low residual admittance required for accurate permittivity measurements and also generates the balanced field that is necessary to solve ground-loop problems. The
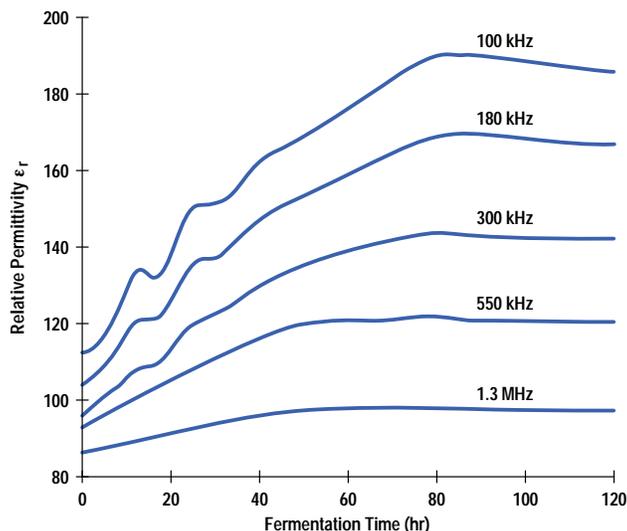
***Fig. 15.** Permittivity changes in beer fermentation (courtesy of T. Yonezawa, Suntory Ltd.).*

corrections make it possible to extract the small capacitive component accurately from an almost entirely conductive admittance.

Acknowledgments

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