INTRODUCTION

The aim of this chapter is to outline some major trends in the continuous stream of papers which describe new methods for investigating or using the electrical properties of dielectrics. In view of the rather large number of collected references, we have been led to select nine most representative topics of the 1976 literature, making it possible to file the various papers.

The first four topics considered all deal with complex permittivity measurements but for different frequency, temperature, and pressure ranges. The development of very accurate interferometric techniques at millimeter and submillimeter wavelengths has led to very valuable papers and impressive results, but microwave measurements still appear as a very active research area mainly due to the continuing development of time domain methods and refinements of cavity techniques. High pressure measurements are also improving and becoming more widely used.

We have deliberately omitted a review in the present chapter of such high electric field specific phenomena as: breakdown experiments, partial discharge, and corona ..., which are to be covered by five other chapters of the present issue. However, various other effects relevant to the so-called high field molecular electrostatics have been considered. Interest is presently reviving in measurement techniques under high electrical fields and there is no doubt that molecular biophysicists will greatly welcome such worthwhile efforts.

Concerning biological systems, electrical noise analysis by correlation techniques has recently proved to be a valuable tool for investigating ion transport processes across biomembranes. On the other hand, high
power microwave irradiation of biomaterials seems to be an attractive area of research on account of very fast, local dielectric heating processes and, possibly, other specific phenomena.

Dielectric materials are in many respects playing a central role in microwave instrumentation, and considerable work is being done in the fields of microwave or millimeter-wave integrated circuits and of applicators for microwave heating. Dielectric measurements have also been used for many years in materials testing, and several new attempts have again been reported in 1976, a number of them dealing with testing humidity of materials.

The references quoted in the bibliography section have been gathered from the Physical Abstracts and the Chemical Abstracts or directly from the literature. Accounting for the inherent relaxation time of these Abstracts, a few relevant 1975 references have been included as a complement to the bibliography of the 1975 digest.

LOW-, MEDIUM-, AND HIGH-FREQUENCY MEASUREMENTS OF DIELECTRIC PROPERTIES

Permittivity of Low-Loss Materials

A transformer bridge operating at 10 kHz, suitable for measurements of the temperature dependence of the relative permittivities of gases was developed by Bergstrom et al. (1). Reported sensitivity is 2 parts in $10^8$.

Permittivity of Conducting Systems

Using a commercial measuring bridge in conjunction with a home-made cell, van Beek et al. (4) were able to measure the permittivity of conducting solutions with a precision better than 1%. For solutions exhibiting specific conductivities of 1/Ω m, the method is limited to frequencies lying between 5-20 MHz, but is applicable in the range 1-100 MHz for specific conductivities smaller than 0.1/Ω m.

An apparatus able to resolve differences as small as one part in $10^5$ in the impedance modulus of two identical cells over the frequency range 0.1-500 Hz has been described by Bernengo et al. (7). Electrode polarization errors are eliminated by using two four-electrode cells.
The transient response of a dielectric to a step function has been used by Le Traon et al. (11) for estimating both the static permittivity and the conductivity. A very promising way of extending time domain spectroscopy towards the low frequencies has been proposed by Husimi and Wada (12). The recorded response function of a sample solution to a binary pseudo-random noise generated by a minicomputer is Fourier transformed, multiplied by the Fourier transform of the binary pseudo-random noise and normalized. The complex permittivity is easily related to the obtained transfer function. The method, the performance of which has been checked on a poly-γ-benzyl-L-glutamate solution, is presently limited to the frequency range 71 Hz-36 kHz, but new developments are suggested which should allow its extension up to the MHz region. A four-electrode cell would obviate the problem of electrode polarization in the case of conducting solutions.

Miscellaneous Impedance Measurements

A bridge featuring a lock-in amplifier as null detector was described by Greve (16) for measuring the low-frequency capacitance of a conducting device. An accuracy of ±0.2% can be achieved. A phase lock technique requiring a lock-in detector and a stable Q-meter with analog output proportional to Q was proposed by Kanazawa and Schoenes (17) for measuring conductance changes to one part in $10^6$ at MHz frequencies on the basis of a method previously used in NMR. Moron (18) has tested an efficient circuit for temperature compensation of a commercial conductivity-meter.

An attractive technique requiring no complex equipment and using Lissajous figures has been developed by Baker and Piercy (19) for measuring complex ac conductivities at frequencies below one Hz. This apparatus allows one to measure nonlinear properties and is adaptable for automatic computer analysis. As shown by Lakes and Harper (20), an appropriate bridge circuit can be designed for measuring the dielectric function in the low frequency domain (0.01 Hz-1 kHz) or for studying step function responses in the time domain.
MILLIMETER-WAVE AND MICROWAVE MEASUREMENTS OF COMPLEX PERMITTIVITY

General

Krueger et al. (31) have investigated the influence of high order mode propagation upon the accuracy of complex permittivity determination in electrolyte solutions. Following their estimation this accuracy is inherently limited to 0.1% because of spurious mode excitation.

Interferometry

Bottreau et al. (38) have described the careful realization of a reflecto-interferometer working at 70 GHz and specifically designed for measuring the complex permittivity of lossy liquids over a wide temperature range (-20°C to 150°C). Stumper and Frentrup (41) have built with standard waveguide components two very accurate interferometers to be used to study very low-loss liquids (\(\tan \delta \sim 10^{-4}\)) at 9 and 29 GHz. The reported uncertainty in \(\tan \delta\) is very impressive (less than \(1.2 \times 10^{-5}\)) and excellent agreement with microwave cavity measurements was recorded.

Cavities and Open Resonators

In order to achieve higher spatial resolution in laboratory scale or atmospheric refractometry, it was desirable to reduce the sampling volume of the usual X-band cavities. A suitable spherical refractometer operating at 36.5 GHz has been designed by Ward and Cole (44): a loading Q of 11,000 was obtained for a sampling volume of only 3.7 cm³. Open resonators are indeed well suited for measuring the complex permittivity of low-loss materials at millimeter or submillimeter wavelengths. Jones (45) was able to obtain very accurate results on isotropic low-loss materials such as tetrafluoroethylene (PTFE), and even to measure the anisotropy of stretched polymers or uniaxial crystals (46). His apparatus is an open hemispherical resonator consisting of a concave and a planar mirror, the sample being inserted on the planar mirror. Typical Q values of 160,000 were obtained at a resonant length of 133 mm when operating at 35 GHz. Standard deviations on losses lying in the range 50-500 \(\mu\)rad and on permittivity were estimated to \(\pm 2\% + 1\ \mu\)rad and 0.1%, respectively. A
MILLIMETER-WAVE AND MICROWAVE MEASUREMENTS

correction taking into account the additional volume of sample extending beyond the curved phase front normally assumed in the beam wave theory has been suggested by Cook and Jones (47). The applicability of the open resonator technique has been extended up to 140 GHz by the same authors (48). Very similar hemispherical resonators were used by Chan Song Lint and Priou (49) for characterizing magnetic materials in the 36-90 GHz range. Another open resonator was also used up to the submillimeter range by Volkov et al. (50).

There is presently an acute need appearing for data at cryogenic temperatures on materials suitable for telecommunication applications or microwave technology. However, as one expects the losses to decrease dramatically at very low temperatures (52), it is clear that special techniques had to be developed for measuring these very low losses. Using a very sophisticated superconducting resonant cavity (machined from high purity niobium and carefully cleaned) Isagawa (53) has been able to measure at 1.3°K a tan δ value as low as 2.4 x 10^-6 for PTFE at 6.5 GHz.

Microwave cavities even offer some interesting possibilities to evaluate quickly the dielectric properties of lossy materials. Developing a method originally suggested by Barlow fifteen years ago, Kumar (55) has measured the complex permittivity at 9 GHz of a few lossy liquids using a resonant cavity which was coupled through one of its end plates to a circular evanescent waveguide. The changes in both the resonance frequency and Q-factor of the cavity on filling the circular waveguide with the investigated material can be related to its permittivity. Sheets of lossy solids have also been studied by the same technique (56). As shown by Hallenga (57) small differences in the dielectric properties of high-loss liquids can be determined with a resolution of one part in 10^4 by resonance perturbation techniques. Another interesting method which is relatively simple to use and apparently yields quick results up to 4 GHz on very lossy materials or even biological tissues has been recently presented by Tanabe and Joines (58). Their method is based on perturbing the fringing field at the open end of a transmission line resonator. Agreement within 5% with current data gathered from the literature is reported.
Time Domain Spectroscopy

An innovative approach which challenges previous determinations of complex permittivity consists in analyzing electric response of systems to fast rising pulses with a resolution of a few picoseconds. The second panel conference on the possibilities offered by this technique was recently held at Bordeaux (68) and the difficulties to be encountered in developing these experiments have been outlined by successive contributors (69, 70). A detailed discussion of the random and systematic errors associated with this technique, and the data reduction has been given by Loeb (71) and Balland (72). Different ways for solving the transcendental reflection equation have been investigated by Roussy and Bourlier (73) and Kent (74), the latter making use of the well-known Newton-Raphson method. As illustrated by the results presented, time domain spectroscopy appears attractive mostly for lossy liquids (75, 76), conductive materials (77) and even biological tissues such as human skin (78), but it is also applicable to rather low-loss materials (79).

By applying a straightforward input admittance analysis to three most interesting circuit configurations and by introducing iterative approximations, Cole (80, 81) derived simple expressions allowing the evaluation of complex permittivity and, where relevant, the magnetic permeability of dielectric materials. Precautions to be taken for conducting systems are also described. As discussed in an early step of Cole's method, it is possible to unravel the dielectric response function directly from time domain experiments without recourse to any Fourier transform. Chahine and Bose (82) have refined this approach by considering higher order corrections in Cole's iterative approximations.

It is well-known that serious truncation errors are to be expected when non-time limited signals are Fourier transformed as, for instance, in the case of conducting systems. Gestblom and Noreland (83) have compared for such systems the respective performances of the Shannon-Samulon formula and of an extended form of Cole's polygon approximation for various sampling densities, and they have shown the Samulon formula to be superior. Another elegant solution to the same problem is to use the windowing algorithm of Gans and Andrews (84).

Homomorphic deconvolution has been shown useful by Riad and Nahman (85) for separating overlapping reflection signals in time domain reflectometry. The method basically
COMPLEX REFRACTIVE INDEX MEASUREMENTS

uses the property of the logarithmic operator to transform a product into a sum in the frequency domain. From a more technical point of view, it has been recognized by Elliott (89) that considerable improvement in the sensitivity of time domain reflectometry could be achieved by eliminating the slow drift of the time window which precludes the use of long term averaging directly. Two methods are proposed: the first one combines a lock-in amplifier with a signal averager and the second requires two lock-ins. The second method appears as the most sensitive, but is only suitable for measuring reflections from a single point.

COMPLEX REFRACTIVE INDEX MEASUREMENTS AT SUBMILLIMETER WAVELENGTHS

Afsar et al. (103) have given an authoritative review on the recent advances in far-infrared spectroscopy which now allow the dielectrician to measure the complex refractive index of almost any material in the frequency range 100 GHz-18 THz. Among the most impressive results reported by the group working at the National Physical Laboratory (UK), are those obtained by Fourier transform interferometry on heavily absorbing liquids such as water or methanol, and also those on very low-loss liquids such as cyclohexane. The description of the techniques, and, more specifically, of the interferometers used for these experiments, is detailed in separate papers (104, 105). The quality or even the feasibility of these measurements seems to have been conditioned by several factors: the use of phase modulation, wire grid polarizing beam splitter, helium cooled Rollin detector, a better design of the experimental cells, and, as shown below, improvement in the data reduction.

As emphasized by Passchier et al. (106), the actual computation of the complex refractive index spectrum with Fourier transform interferometry is not straightforward, but very useful general expressions can be derived for free layer experiments or for windowed liquid cells featuring a variable thickness. The same group at Leyden has presented a cogent error analysis of free layer experiments (107) and stressed that error due to the vapor above the liquid specimen can be quite substantial. In a cooperative action with the NPL group (108) they have also shown that accurate complex refractive index spectra can be determined in the far-infrared regions 5-500 cm⁻¹, even for absorbing liquids, from dispersive interferograms obtained with a variable thickness, variable temperature cell containing the liquid specimen.
Dispersive reflection spectroscopy has also been carried out on solids between 77°C and 300°C by Ledsham et al. (110) using a polarizing interferometer, and good agreement with earlier data has been reported. Birch et al. (111) have performed dispersive Fourier transform measurements on fully opaque solids at 300°C, and have described a powerful two beam interferometer.

From a more technical point of view, Meyer and Lagarde (116) have shown that far-infrared radiation emitted by the storage ring ACO of the linear accelerator at Orsay might be a competitive source for Fourier transform spectroscopy down to the millimeter range, on account of the high intensity and low noise characteristics of this radiation. Continuing interest still exists for spot measurements with optically pumped FIR lasers as illustrated by the work of Bean and Perkowitz (117).

TEMPERATURE AND PRESSURE DEPENDENT PHENOMENA

Thermally Stimulated Discharge Currents

Thermally stimulated depolarization is now becoming widely used to complement the conventional dielectric relaxation measurements on polymers and in supercooled rotator phase studies. A comprehensive and most authoritative book by van Turnhout (119) on thermally stimulated discharge of polymer electrets made a welcome appearance.

Measurements over a wide range of temperature in supercooled phases are often difficult due to the lack of convenient cell featuring a good response to cooling or heating. Jones et al. (120) have described two possible configurations for such a cell. Both are easy to construct and to operate. Using one of them, they have been able to cool down cyclohexanol from 200°C to 149°C in less than three minutes.

High Pressure Permittivity Measurements

Interest is growing in measuring the static and dynamic dielectric properties of gases and liquids at high pressures. Using a very stable cylindrical capacitor, Weber (130) has measured the static permittivity of liquid and gaseous ethane up to $3.9 \times 10^7$ Pa over the temperature range 95°C-323°C, with an estimated accuracy of 0.01%.
It has been recognized by Scaife and Vij (131) that the combined effect of lead inductance together with the shunt capacitance of the test sample can give rise to fairly large errors in high pressure bridge measurements at MHz frequencies. Suitable corrections have been proposed which account quite successfully for these errors. Yakushev et al. (137) have described a method for measuring at 9 MHz the static permittivity of materials at high dynamic pressure with a time resolution of $10^{-7}$ s and an estimated error of less than 2%.

Nonlinear Permittivity Measurements

Several types of nonlinear dielectric behavior under the action of high fields are known and have been recently reviewed by Davies (141). Of particular interest is the class of nonlinear dielectric phenomena which are characterized by field induced perturbations of chemical equilibria (142). The hypothesis of tautomeric equilibria in hydrogen-bonded systems has been reinvestigated by Malecki (143) with the help of nonlinear static dielectric measurements. The apparatus used for these experiments is described and is an improved version of Malecki's well-known original setup.

Hellemans and de Maeyer (145) have proposed a new differential technique for measuring dynamic nonlinear dielectric effects in solution over the range 2-100 MHz. A low-frequency field of high amplitude, and a swept high-frequency field of low amplitude are applied simultaneously to a sample contained in a capacitance included in a resonant circuit. While slowly sweeping the hf generator, a signal corresponding to the second harmonic of the high-field frequency is detected and recorded; it is proportional to the difference between resonance curves with and without field. Very impressive measurements on $\varepsilon$-caprolactam/cyclohexane solutions have revealed that the high-field induced increments of complex permittivity relax approximatively as a Debye process, but interpretations of the molecular mechanisms underlying this result are still uncertain.

An experimental arrangement has been described by Meskauskas and Grigas (147) for determining the nonlinearity of the complex permittivity of antimony (II) sulfide iodide in the microwave region by means of second
harmonic generation for microwave fields of typically 2-50 kV/m (20-500 V/cm).

Nonlinear Conductivity Measurement (Wien Effect)

Nauwelaers et al. (150) have detailed the realization of a high-field, high-frequency modulation apparatus suitable for measuring the frequency dispersion of the Wien effect in solution; the great potential of this new relaxation technique for studying the chemical relaxation of ion-pairing processes is demonstrated.

Liquid Crystals

Ikeno et al. (167) have studied the dielectric relaxation of liquid crystals under dc electric fields.

ELECTRICAL PROPERTIES OF BIOMATERIALS

Electrical Noise Correlation in Biomembranes

It was realized recently that the small electrical fluctuations occurring at the nerve membrane level could also provide a novel insight in the microscopic mechanism of ionic conduction in these systems. This possibility has been reviewed by Conti and Wanke (172).

An experimental setup for electrical noise correlation measurement has been detailed by Kolb et al. (173) who have tried to use this technique for investigating kinetics of gramicidin A channels. Similarly Moore and Neher (174) brought it to bear on the problem of the moniazomycin induced conductance in black lipid membranes, and it was recognized that the conventional pulse response technique and the fluctuation analysis do not yield the same informations. The great potential of the fluctuation method is also emphasized by the recent work due to Molenaar et al. (175) on membrane noise in Paramecium. These authors report that the noise voltage seems to be filtered by a resonance like membrane impedance and suggest an interpretation of the phenomenon.
Microwave Techniques

Considerable attention is being paid to the influence of microwave radiation on biological tissues, and stimulating conditions are created for the study of the dielectric properties of biomaterials in the microwave and millimeter-wave region.

Edrich and Hardee (182) have reported the first investigation by a phase-less technique of the complex permittivity and penetration depth $\delta$ of muscles and fat tissues between 40 and 90 GHz. The relatively large values observed for $\delta$ make millimetric thermography particularly attractive.

Another interesting problem lies in determining the interior field of irradiated biological materials; a useful approach to the problem was proposed by Brodwin et al. (184). It was also reported that very fast and local microwave dielectric heating allowed to fix brain enzymes in situ (190, 191).

DIELECTRIC MATERIALS AND MICROWAVE TECHNOLOGY

Microwave Integrated Circuits and Dielectric Waveguides

Knox (195) was invited recently to give a panel paper on the dielectric waveguide microwave integrated circuits. A major, and not surprising, trend in the field is the rapid development of millimeter-wave integrated circuit technology.

Itoh (196) has described a new type of dielectric waveguide (inverted strip) suitable for millimeter-wave propagation. This new circuit consists of a guiding layer placed on a dielectric strip which in turn sits on a ground plane. A novel technique was used for measuring the field distribution of this structure in the 80 GHz range. In another paper, Samardzija and Itoh (197) have discussed a different dielectric waveguide structure called double layered slot line, in which the conventional slot line is modified by introducing an additional dielectric layer between the ground plate and the substrate. The propagation characteristics of this new structure were investigated by the Galerkin method.
Microwave Dielectric Heating

Direct production of thermal energy inside a dielectric can be achieved by microwave irradiation as a consequence of the overall dipolar relaxation losses. A primary reason for preferring microwave to rf heating is often associated with the superior filling factors obtained at microwave wavelengths. However, specific applicators have to be designed for each problem if the maximum efficiency is to be reached.

Berteaud and Badot (227) were able to generate high temperatures in refractory materials. Elemental sulphur was oxidized to sulfuric acid in aqueous phase by microwave heating, as reported by Vuorinen and Bruce (228). Another apparatus for heating nylon filaments has been designed by Huang (231). A cylindrical waveguide applicator with an uniform power density distribution over its cross section has been described by Gupta (232).

TESTING

An improved automatic digital microwave hygrometer which requires no moving parts has been designed at the National Bureau of Standards by Stokesberry and Hasegawa (237). The method relies on a comparison of the resonance frequencies of two cavities.

New approaches to test insulating oils have been discussed by Burns (239). It is suggested that measuring relative humidity provides much more meaningful data than measuring the water content in parts per million.

Bosisio and Huy (242) have proposed a simple and useful method for finding out the amount of solid material that is present with water in a given test sample on which moisture content testing has to be done. Dielectric measurements are carried out before and after a liquid nitrogen freeze-drying.

STANDARDS AND CALIBRATION

An appraisal of tests and standards for the evaluation of electrical insulating fluids has been defined by Miller et al. (270).
Acknowledgements

The authors are indebted to Dr. G. Roussy for facilities in preparing this review.

BIBLIOGRAPHY

An asterisk precedes papers not explicitly discussed in the text.
The topical outline follows that of the text.

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Miscellaneous Impedance Measurements


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