Prof. Graham Williams:

**Dielectric and electrical properties of materials**

The dielectric and electrical properties of insulating and semiconducting dielectric materials as measured over wide ranges of frequency and temperature have been the subject of considerable interest in recent years.

In terms of the measurements, a sample in the frequency range $10^{-6}$ to $10^{8}$ Hz is regarded as a lumped-circuit element having a frequency-dependent complex impedance $Z(f)$ while at higher frequencies, ranging from the UHF through the microwave range to the far infra-red region, i.e. $10^{8}$ to $10^{12}$ Hz a sample is regarded as a distributed circuit element having a frequency-dependent complex propagation coefficient $\gamma(f)$.

Experimental data, in terms of $Z(f)$ of $\gamma(f)$, covering the entire frequency range $10^{-6}$ to $10^{12}$ Hz may be re-expressed in different ways. Traditionally, different areas of research have used different derived quantities as is shown in table 1.

Thus dielectric properties, expressed in terms of $\varepsilon(f)$, are used when studying molecular motion in solid polymers while electrical properties expressed in terms of $Z(f)$, $M(f)$ or $\gamma(f)$ are used when studying conduction processes in ionic solids or liquid electrolytes, etc. etc. It is important to stress that the electrical/dielectrical properties of a material can be expressed in these different ways and one should remember that a particular representation can be converted into any other e.g. $Y=1/Z$, $M=1/\varepsilon$ etc.

As a result, different approaches to the electrical/dielectric properties of materials have been made over the years and their inter-relationships have been neglected. Dielectrics Relaxation (using $\varepsilon$), Impedance Spectroscopy (using $Z$) and Electrical Relaxation Spectroscopy (using $M$) are all inter-related since the experiments actually measure $Z (=1/Y)$ in all cases. This is being appreciated increasingly so we should accept that apparently-different researches are actually inter-related and that the electrical quantities used are a matter of choice, based on prior knowledge of the electrical/dielectric phenomena that may be involved in each case.

Having noted the different representations that are presently used for the electrical/dielectric properties of materials, we observe that up to about ten years ago most experimental studies of materials were made over limited frequency bands by a manual point-by-point procedure.

Thus, typically, using a low frequency bridge, measurements at 16 frequencies equally-spaced in the log $10^{-5}$ scale would take up to 30 minutes to complete. While the measurements were accurate, the inability to obtain data quickly severely hampered the use of dielectric relaxation spectroscopy (DRS) or its equivalents impedance spectroscopy (IS) and electrical relaxation spectroscopy (ERS). At the same time rapid advances were being made in other physical methods such as nuclear magnetic resonance (NMR) relaxation spectroscopy, electron-spin resonance (ESR) spectroscopy, quasi-elastic light scattering (QELS), Fourier transform infra-red spectroscopy (FTIR) and fluorescence depolarization (FD). These methods are often complementary to DRS for studying physical processes in materials.

Fortunately, the situation has changed dramatically during the past ten years. The arrival of fast accurate impedance analyzers, frequency response analyzers and **new technologies now available**

pulsed-transient equipment for the range $10^{-6}$ to $10^{6}$ Hz and fast accurate network analyzers and time-domain reflectometry equipment for the range $10^{8}$ to $10^{10}$ Hz together with the computer control of measurement, data acquisition and data-processing and computer control of sample temperature has enabled DRS, IS and ERS to take their rightful place alongside NMR, ESR, QELS and FD in the range of modern methods used to study the physical properties of materials.

Commercial equipment is now available which provides fast accurate measurements of the dielectric/electrical properties of liquid and solid materials over a range of prescribed temperatures and frequencies, where the measurements are made automatically and the data are processed on-line into any convenient form.

Such equipment is provided, for example, by the range of NOVOCONTROL dielectric spectrometers each working over a wide frequency band i.e. $10^{-5}$ to $10^{7}$ Hz, $10^{5}$ - $10^{9}$ Hz and $10^{9}$ - $10^{10}$ Hz.
Measured Quantity | Symbol | Application
--- | --- | ---
Impedance | Z = R + iX  
R = Resistance  
X = Reactance | Conduction in ionic liquids and solids, polymer electrolytes, semiconductors
Admittance | Y = G + iX'  
G = Conductance  
X' = inverse reactance | As for impedance
Permittivity | ε = ε' - ie"  
ε' = real permittivity  
ε" = loss factor | Dielectric relaxation in dipolar liquids, liquid crystals and solids, polymers and glass forming liquids
Dielectric Modules | M = M' + iM" | Electrical relaxation in ionic liquids and solids, electrolytes, molten salts, semiconductors
Electrical Conductivity | σ = σ' + iσ"  
σ' = real conductivity | Conduction in ionic liquids and solids, semiconductors
Complex Propagation Coefficient at wavelength λ₀, Complex refractive index n | γ = α + iβ  
α = attenuation factor  
β = 2πn/λ₀  
n = n' + in" | Dielectric and far infra-red absorption in dipolar liquids and solids

Table 1

The availability of such modern equipment makes possible high quality research into the dielectrical/electrical properties of a wide range of organic and inorganic materials - as an extension of earlier work - and of new functional materials that are of importance in relation to their electrical, dielectric, electro-optical and conduction properties.

In addition, measurements are now possible, through the speed and practical convenience of the modern techniques, with systems that were not feasible using the traditional manual point-by-point methods.

real-time dielectric spectroscopy

In particular, the techniques of real-time dielectric spectroscopy is emerging as a means of studying the dielectric/electrical behaviour of materials whose physical or chemical properties are changing with time. In this case the dielectric permittivity ε(f) is determined across a frequency range by continual sweeping and recording the time of each measurement, yielding ε'(f,t) and ε"(f,t) throughout the time-dependent process. Post-processing of data allows (ε',ε") values to be determined as a function of frequency at given times t. Such studies open up an entirely new domain of application of modern dielectric-relaxation spectroscopy, especially for polymerizing organic systems. Similar time-dependent dielectric/electrical phenomena may be envisaged for inorganic materials (e.g. the dynamics of phase-transformations in inorganic solids).

Table 2 shows examples of materials and t-dependent system that are being studied using modern techniques:

1. Amorphous Organic And Inorganic Materials
Molecular liquids including glass-forming liquids, amorphous polymers, semiconductors and photoconductors, liquid, solid and polymer electrolytes, ionic liquids, molten salts and glassy ionic solids.

2. Liquid-crystalline Materials
Low molar mass and polymeric thermotropic liquid crystals including nematic, smectic, chiral-nematic and ferroelectric materials, lyotropic liquid crystals including rod-like polymers or surfactants with solvents, hybrid liquid-crystalline polymer networks, polymer-dispersed liquid crystals.

3. Crystalline Material
Ionic crystals as insulators, semiconductors and electrolytes, molecular crystals including rotator-phase crystals and crystalline polymers, ferroelectric crystals, crystalline semiconductors and photoconductors.

4. Time-dependent Systems
Systems undergoing bulk polymerization e.g. thermosets, bulk addition polymerization by thermal or photochemical initiation, systems undergoing crystallization e.g. crystallizing
polymers, systems undergoing phase separation e.g. polymer mixtures at elevated temperatures.

Particular interest in the future is likely to be given to the dielectric and electro-optical properties of liquid crystals, novel hybrid organic liquid-crystal-polymer-networks and polymer-dispersed liquid crystalline display materials

**what comes next?**

where the dielectric properties will vary with an applied AC or DC biasing field. Such behaviour has been studied extensively by Kremer (Mainz / Leipzig) for ferroelectric crystals and has given important information on the mechanisms for the electro-optical response in such materials.

The nature of charge motion, and its associated relaxation, in inorganic and organic semiconductors and photoconductors may be investigated using broadband DRS, or its equivalents IS and ERS, and this is an area to which the modern equipment will be applied increasingly.

It is clear that the availability of modern equipment capable of making fast accurate measurements of dielectric / electrical properties of the range of materials shown in table 2 will stimulate an expansion in dielectrics research for time-dependent and time-independent systems. The expansion in research activity in the frequency range $10^{-3}$ to $10^{7}$ Hz is already apparent in the literature but the use of the higher frequency range $10^{8}$ to $10^{10}$ Hz is in its infancy and we await new studies in this little-explored region for the materials and systems described in table 2.

The writer has been active in dielectrics research for nearly forty years and for much of that time has laboured, with his students, to obtain comprehensive dielectric data for amorphous and crystalline polymers and glass-forming liquids using the traditional point-by-point method of measurement. His former supervisor, Professor Mansel Davies, remarked in the early 1960's that any expansion of dielectrics research would only occur when commercial dielectric measuring assemblies became available.

It has taken over 30 years for that to be achieved and we can now say with complete confidence that the modern broadband dielectric spectrometers will enable research into the dielectric and conduction properties of materials of all kinds to be conducted quickly, accurately and conveniently at the highest professional level to yield information that is crucial to our understanding of polarization and charge transport processes in both conventional materials and the new classes of novel electroactive and photoactive materials now being provided for modern technology.

Prof. Graham Williams
Department of Chemistry
University College of Swansea
Singleton Park,
Swansea SA2 8PP, U.K.

**Prof. Friedrich Kremer:**

**Dielectric spectroscopy: Old spectroscopic technique gains new actuality**

Dielectric spectroscopy is an old spectroscopic technique, which has roots going back to the last century. Claurius, Mosotti, Lorenz, Maxwell - just to mention some of the pioneers - made important contributions to the understanding of electrical and dielectric phenomena.

In the second decade of this century Debye formulated the theory of dielectric dispersion which is outlined in his famous book on "Polar Molecules". This formed the basis of a microscopic understanding of dielectric relaxation processes, which was refined later by Kirkwood, Fröhlich, Onsager and Cole.

**new actuality**

Nowadays, dielectric spectroscopy is gaining new actuality. In its modern form it covers easily more than 12 decades in frequency. For that, different measurement systems based on different physical measurement principles have to be combined (see below). This outstanding dynamic range makes dielectric methodology especially valuable as a spectroscopic tool. Studies on the scaling of relaxation processes, on the dynamic of liquid crystals or the frequency dependence of charge transport in (polymeric) semiconductors are based on the huge frequency window which is readily accessible with modern equipment.

**modern impedance analyzers save time**

A more practical advantage of dielectric spectroscopy results from the measurement speed of modern impedance analyzers, e.g. a frequency sweep from $10^6$ Hz to
This opens complete new fields of research, for instance the fast monitoring of chemical reactions, the control of cure in thermosets, the monitoring of charge transport, etc. In modern production control dielectric methods play a significant role.

A further advantage of dielectric spectroscopy results from the fact that the capacitance of a sample capacitor is inversely proportional to its thickness. Hence, as long as a sample material can be prepared as an (ultra)-thin capacitor, the sensitivity of the measurement is increasing with decreasing thickness, i.e. decreasing amount of sample material. This aspect is of special importance in modern materials sciences, where newly synthesised materials are often obtained in mg quantities only.

Last not least: Compared to other spectroscopic techniques like Nuclear Magnetic Resonance, dynamic light scattering or dynamic mechanical spectroscopy, dielectric methods are much less expensive.

Prof. Dr. Friedrich Kremer
Universität Leipzig
Fakultät für Physik und Geowissenschaften
Linéstraße 5
04103 Leipzig, Germany

Dr. Gerhard Schaumberg
Overview: Modern measurement techniques in Broadband Dielectric Spectroscopy

This article is the first of a series about modern measurement techniques in broadband dielectric spectroscopy. Its intention is to give an overview about the most common techniques currently available and to show which is convenient for particular measurement problems. Each of the techniques will be discussed in detail in the following newsletters.

Broadband dielectric spectroscopy measures the complex dielectric function \( \varepsilon = \varepsilon' - i \varepsilon'' \) of materials in dependence on frequency. \( \varepsilon \) reflects the molecular relaxation and transport processes of the material, which depend on nearly any other physical quantity like e.g. temperature, time, superimposed electromagnetic fields, pressure, etc. Therefore applications in science and technology seem to be almost unlimited. Some examples for scientific applications are studies of the:

- studies on the molecular dynamics of liquids, liquid crystals and polymers,
- charge transport in semiconductors, organic crystals, ceramics, etc.,
- monitoring of chemical reactions or polymerization processes,
- structural material properties like phase compositions, phase transitions and crystallization processes,
- non-linear electrical and optical effects.

Industrial applications are in quality control, characterization of isolating materials and semiconductors. Materials changing their dielectric function if exposed to gases or liquids are used in sensor applications.

Broadband dielectric spectroscopy links up with optical and IR-spectroscopy for the low frequency region between \( 10^{11} \) and \( 10^5 \) Hz. The material under test generally is placed between two electrodes forming a kind of capacitor as sketched in fig. 1.

The sample capacitors impedance \( Z_S \) is connected to the dielectric function by

\[
\varepsilon = \varepsilon' - i \varepsilon'' = -\frac{i}{2 \pi f Z_0 C_0} \tag{1}
\]

where \( f \) denotes frequency and \( C_0 \) is the vacuum capacity of the sample capacitor. In most cases, \( \varepsilon \) is measured as a function of two or even three parameters (e.g. frequency, temperature, DC-bias). As these multi dimensional measurements produce large amounts of data and also long measurements times are involved, automatical measurement systems are required.

Therefore, a dielectric spectrometer generally consists of the following components:

- a sample cell with the sample capacitor,
- a system being able to measure the complex impedance of the sample capacitor over a wide frequency and impedance range with high precision,
- a system allowing to expose the sample capacitor to other physical quantities like temperature, DC-bias, etc.,
- a computer which controls the measurement flow, the compatibility of the devices and the evaluation of the measured data.
In addition, special techniques and equipment to prepare the sample capacitor may be required. The impedance $Z_S$ of the sample capacitor may be determined either from a measurement in the time domain or in the frequency domain.

In the time domain, the sample is excited with a short voltage pulse or step and the decreasing sample current $I(t)$ is measured as a function of time. The impedance $Z_S(f)$ in the frequency range is calculated by means of a discrete Fourier transformation. The advantage of this technique, is that it is as fast as in principle possible. On the other hand, it is sensitive to electrical disturbance like noise and leakage currents, and requires high speed electronics at frequencies above 10 kHz. For these reasons measurements in the time domain are generally less accurate than in the frequency domain. The time domain will be discussed in detail in a later Dielectrics Newsletter.

This paper will focus on the frequency domain, where the sample is excited with a harmonic signal $U_S(f)$ at the measurement frequency. $Z_S$ is determined by sensing the amplitude of the sample current with respect to $U_S(f)$. Depending on the frequency range, frequency response analysis, AC-bridge methods or coaxial line reflectometry is providing the best results.

Frequency response analysis covers the range from $10^{-5}$ - $10^7$ Hz with high precision. The sample current $I_S(f)$, the sample voltage $U_S(f)$ and the phase shift between them are measured directly. The sample impedance is calculated from

$$Z = Z' + iZ'' = \frac{U_S}{I_S}$$  \hspace{1cm} (2)

where $U_S$ and $I_S$ are written in complex notation. The principle arrangement is shown in fig. 2. The generator drives the sample with the voltage $U_S$, being directly measured with Ch I of a vector voltage analyzer (VVA). $I_S$ is measured with VVA's Ch II after it has been transformed by a current to voltage converter. The VVA is using the same principle as lock-in amplifiers. Two internal harmonic reference signals being shifted by 90° in phase are multiplied with the measured signal. After averaging over many periods, both signals correspond directly to the input signal's real and imaginary parts. An additional advantage of this technique is that all harmonic components that differ from the measurement frequency are suppressed. Therefore frequency response analysis is not sensitive to noise or non linear distortions.

In modern systems like the NOVOCONTROL BDS 40, the current to voltage converter is mounted in an active head directly above the sample cell. As a result of that, errors caused by the measurement cables at high frequencies are minimized. In addition to this, each sample measurement is compared to a reference capacitor which is automatically adjusted close to the sample impedance. This allows the elimination of all linear errors in the whole system.

The system operates fully automatic at frequencies from $10^{-5}$ - $10^7$ Hz with a resolution in $\tan(\delta) < 10^{-5}$ and covers an impedance range from $10^{-1}$ - $10^{14}$ Ω. It is particularly suited for sophisticated applications in scientific or industrial research where high precision and a large frequency range is required.

AC-bridge methods cover the frequency range from 10 Hz - 10 MHz with medium precision. They can be seen as an economical alternative to the frequency
In balanced state, the damping constant $\gamma$ is $< 5 \times 10^{-4}$.

The wavelength $\lambda$ is calculated by $\lambda = \frac{c}{f}$, where $c$ is the speed of light and $f$ is the frequency.

Response analysis for applications in which low frequency measurements are not important. The principle of measurement is shown in fig. 3.

The impedance bridge consists of the sample capacity and the adjustable compensation impedance $Z_C$. On the left side of the bridge, the generator drives the AC-bridge methods

Sample with the fixed and known AC voltage $U_S$ which causes the current $I_S$ to flow into P1. On the right hand side of the bridge, the variable amplitude - phase generator (VAPG) feeds the current $I_C$ through the compensation impedance $Z_C$ into P1. The bridge will be balanced, if $I_C = I_S$ which corresponds to $I_0 = 0$. Any deviation is detected by the zero voltage detector which changes the amplitude and phase of the VAPG as long as $I_0 \neq 0$. In balanced state, the sample impedance is calculated by

$$Z_S = \frac{U_S}{I_S} = \frac{U_S}{U_C} Z_C \quad (3)$$

Automatic bridges which are also used in NOVOCONTROL dielectric measurement systems are HP 4284 (20 Hz - 1 MHz, resolution tan(δ) < 5 \times 10^{-4}, 1 mΩ - 100 MΩ) and HP 4192 (10 Hz - 10 MHz, resolution tan(δ) < 10^{-3}). For dielectric measurements a standard sample cell is required which is connected by BNC cables to the bridge. In practice the lines shift the high frequency measurement limit to approximately 0.5 MHz. Also the low frequency limit may not be reached except for dielectric samples with high losses (tan(δ) > 1) as the sample impedance exceeds the high impedance measurement limit of the bridge.

Nevertheless AC-impedance bridges offer a suitable and inexpensive solution for applications which do not need a large frequency range. As the measurement time is lower compared with the frequency response analysis, AC-bridges are particularly suited for time dependent monitoring of polymerization processes and chemical reactions. Also applications largely impedance is measured with a microwave reflectometer.

For this purpose, the incoming and reflected waves are separated depending on temperature like characterizations of phase compositions, phase transitions and crystallization processes can be solved by AC-bridge methods successfully.

**coaxial line reflectometry**

Coaxial line geometry can be used at frequencies from 1 MHz - 10 GHz. In contrast to the low frequency techniques already described, above 10 MHz the measurement cables always contribute to the sample impedance. Above approximate 30 MHz standing waves arise at the line and a direct measurement of the sample impedance completely fails. This can be avoided by application of microwave techniques taking the measurement line as the main part of the measured impedance into account. Therefore, precision lines with defined propagation constants are required. The principle of measurement is shown in fig. 4.

The sample capacitor is used as the termination of a precision coaxial line. The complex reflection factor $r(l)$ at the analyzer end of the line depending on the sample with two directional couplers and are phase sensitively measured. $r$ is defined as the ratio of the voltages (or electrical fields) of the reflected wave to the incoming wave on the line. It depends on the location of the measurement on the line.

$$r(x) = \frac{U_{ix}(x)}{U_{0i}(x)} \quad (4)$$

For an ideal line, $r(l)$ which is measured by the reflectometer can be transformed to the reflection factor $r(0)$ at the sample end of the line by

$$r(0) = r(l) e^{2\alpha x + \beta l} \quad (5)$$

where $\alpha$ is the damping constant and $\beta = 2\pi l/\lambda$ ($\lambda$: wavelength) the propagation constant of the line. From (5), the sample impedance is calculated by

$$Z_S = Z_0 \left[ 1 + r(0) \right] \quad (6)$$

where $Z_0$ is the wave resistance of the line. As can be seen from (6), the measurement range is limited to sample impedance $Z_S$ being in the range of $Z_0$. If this is not the case, the reflection $r(0)$ becomes nearly 1 or -1 and the measured $r(l)$ changes only marginally.

In practice, the lines are not ideal
and sophisticated calibration procedures have to be applied. Nevertheless, low loss precision lines matching to the output resistance of the reflectometer are required. The line parameters $\alpha$, $\beta$ must be homogenous over the whole line and also independent of temperature, as the calibration generally can only be carried out at room temperature.

The same criteria mentioned for the line apply to the sample cell. Therefore an additional calibration which eliminates the influence of internal impedances in the sample cell is required.

An example for a commercial system based on the analyzer HP 4191A including the coaxial wave guide, sample cell (shown in fig. 6) and temperature control is the NOVOCONTROL BDS 5000.

In order to keep the wave guide as short as possible, the cryostat with the sample is directly mounted at the front of the analyzer. The system is automatically operated by a computer and all calibrations are done by software.

The frequency range is 1 MHz to 1 GHz with a resolution in $\tan(\delta) < 10^{-3}$ and overlaps with the frequency response analysis methods. This is important, as the accuracy at the borders of the measurement range rapidly decreases.

At frequencies above 1 GHz, network analyzers can be used. Although these devices are specified to work in the millimeter range up to 300 GHz or even higher, calibration procedures become extremely cumbersome above 10 GHz which seems to be the practical limit for dielectric measurements with temperature control. Direct measurements to 60 GHz on substrates using coplanar probe tips are reported in [3].

**References**

/1/ J. C. Slater, Microwave Electronics, D. van Nostrand Company, New York 1950
/2/ P. I. Somlo, J. D. Hunter, Microwave Impedance Measurements, London : Peter Peregrinus 1985

G. Schaumburg; Novocontrol GmbH
Obererbacher Str. 9
56414 Hundsangen, Germany

**Recommended:**

**Literature**


Daniel, V.V., Dielectric Relaxation, Academic Press London 1967


Fröhlich, H., Thory of Dielectrics, Oxford University Press, London 1958

Grant, E.H.; Sheppard, R.J. and South, G.P., Dielectric Behaviour of Biological Molecules in Solution, Oxford University Press 1978

Hedvig, P., Dielectric Spectroscopy of Polymers, Hilger, Bristol 1977


Matsuoka, S., Relaxation Phenomena in Polymers, Hanser, Munich 1992


Takashima S., Electrical Properties of Biopolymers and Membranes, Adam Hilger, Bristol 1989

![Fig. 5: Reflection factors and impedance on a line terminated by the sample impedance.](image1)

![Fig. 6: RF sample cell](image2)
Abstracts and suggestions are always welcome. Send these directly to the publisher.