

Traceable Measurements of the Static Permittivity of Dielectric Reference Liquids at Temperatures from 5 to 50°C using a Micrometer Driven Admittance Cell

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Introduction

Traceability of RF and Microwave dielectric measurements is much facilitated by the use of reference dielectrics and NPL has been pursuing a programme of measurements to make more of these materials available [1]. Both solid and liquid reference materials have their value, but the former suffer from variability of electrical properties from one manufactured batch to another. Reference liquids have the advantage that samples of a high-purity grade taken straight from a newly-opened bottle are very consistent and so their properties can be published for use in the calibration and checking of instruments for complex permittivity measurements.

To suit this purpose liquids having a range of complex permittivities are required. Both non-polar and polar reference liquids are useful, as they have quite different properties. Non-polar liquids (e.g. cyclohexane and silicone oil) generally have low permittivity, low loss, low temperature coefficient and low frequency dependence of permittivity, whereas polar liquids (e.g. alcohols and water) have none of these characteristics. Polar liquids with short-chain molecules (e.g. water, methanol and ethanol) are of value for calibrating and checking high loss, aqueous and particularly biological tissue measurements. Their dielectric behaviour throughout much of the RF and microwave range is conveniently described by dielectric relaxation models, such as the single and multiple Debye models [2, 3]. They allow the complex permittivity to be calculated easily from the relaxation parameters at a specified frequency and temperature. One of the most important of these parameters is the 'static' (i.e. low frequency) permittivity [2, 3].

A limited programme of RF and Microwave measurements on reference liquids was carried out at NPL during the years 1990-1992 [2]. This covered measurements of static permittivity in a micrometer-driven admittance cell and measurements of high-frequency permittivity (up to 3 GHz) in coaxial transmission line cells. The earlier project was limited, however, to a temperature range of 20 - 30°C, which does not encompass the full industrial range of interest, and the number of measurements undertaken was limited by the slowness of the temperature control in the admittance cell. Full experimental details of this earlier work have not previously been published and some of the details are given here for the first time. The current programme extends the earlier work in three ways: (i) the temperature control of the liquid admittance cell has been improved, allowing for faster, more reliable control, (ii) a wider range of temperatures is possible: 5 - 50°C, (iii) a wider range of liquids is being measured. The static permittivity measurements reported here will be followed by RF & Microwave measurements next year. When the work has been completed, results will be published in NPL reports.

The Admittance Cell

Figure 1 is a schematic of the liquid cell as it has now been modified (see [2] for its original form). The principal components are two parallel disc electrodes, H and I in the figure, contained within a cylindrical shield, F, all made from gold-flashed brass. A large-barrel precision micrometer, A, enables the separation between the 40-mm diameter electrodes to be altered, typically over the range 0.3 - 2.3 mm during measurements. The outer screening body of the cell, F, is connected to the screen terminals on the bridge. Metallic bellows, J, ensure complete containment of liquid, while enabling the upper electrode to be moved axially. Water can be circulated through the screening shield, F, to control the temperature. Access holes are provided to allow the temperatures of both electrodes to be measured directly using platinum-resistance thermometers. These are shown *in situ* in the figure but are always retracted during the electrical measurements.

Extension of the practicable temperature range of measurements for the current programme of work required the micrometer to be thermally isolated from the upper electrode by the use of polymer (PEEK) components, C and E. Fine control of the temperature of the upper electrode can be achieved by circulating hot or cold air through a copper coil which is wrapped around the assembly. It is necessary to use air here rather than water since the upper assembly, including the micrometer, is at "high" potential and circulating water would electrically shunt the measurement cell. With these modifications, it was found to be possible to control the temperature to within 0.2°C over the range 5 - 50°C when the cell is filled with liquid.

The cell was originally designed with adjustable electrodes for two reasons: (i) to permit a degree of geometric flexibility to aid in the detection and quantification of systematic errors and (ii) to allow the magnitude of the

electrode polarisation effect [4] to be investigated. This low frequency effect is connected with the inability of the charge carriers in the liquid to pass into the metal electrodes and takes the form of a large and unpredictable series impedance at the liquid/metal interfaces. It can be reduced by using special electrodes (e.g. platinum-iridium) and the cell was designed to take replaceable electrodes for this reason. However the effect falls in magnitude roughly as the square of the frequency and can be made negligible by working at sufficiently high frequencies - in this case 200 kHz - 1 MHz. At these frequencies the real permittivity of the reference liquids differs from the static permittivity by an insignificant amount (see Table 1, below).

The Admittance Bridge

The calibrated and traceable Hewlett-Packard model HP4194A bridge is a four-terminal impedance analyser connected via metre-long coaxial cables to the cell, the "high" bridge terminals being connected at the upper electrode, and the "low" terminals at the lower electrode. Measured capacitances are corrected for the effects of the lead inductance using a lumped impedance model valid up to 1 MHz. Tests were performed to demonstrate that capacitances between the electrodes and screen do not affect the readings significantly (although, if very large, they increase the noise in the measurements). Independence from the capacitance value between the "high" electrode and shield is essential since it varies with the setting of the micrometer.

Experimental Procedure

In principle, the method is a very simple one, being based directly upon the definition of permittivity: the static permittivity is computed from the ratio of the measured capacitance between the electrodes when the cell contains liquid and when it contains air at the same electrode spacing. However, there are a number of reasons why a more elaborate procedure must be followed. These include the fact that the electrode separation for a given micrometer setting varies with temperature and one cannot guarantee to within $\pm 0.1^\circ\text{C}$ that the air and liquid measurements take place at the same temperature. Measurements of capacitance are made over a range of electrode spacings and are extrapolated (by linear regression of reciprocal capacitance vs. micrometer reading) to find the micrometer setting for zero spacing. This procedure is carried out on the air measurement, and on each liquid measurement. This allows an ambient temperature measurement on air to be used as the reference for measurements on liquids at all other temperatures. A number of other corrections and procedures are undertaken to allow for systematic sources of error (e.g. stray capacitance) and non-linearity in curve fitting.

Typically, measurements are made every 0.05 mm over a range of electrode separations from 0.3 mm to 2.3 mm. The bridge is set to measure the capacitance at several frequencies between 200 kHz and 1 MHz and the permittivity is calculated at each micrometer setting and frequency. The overall published result is a weighted average. This average takes into account systematic (type B) uncertainties arising from instrumental effects associated with the admittance bridge.

The temperature of each electrode is measured using the calibrated platinum resistance thermometers. Readings of capacitance are only undertaken when the two readings agree to well within 0.1°C .

Uncertainty Budgets

Table 1 shows a typical uncertainty budget for measurements undertaken with the cell prior to its improvement. At the time of writing the improved budget after modification has not yet been completed, but contributions are either similar to or better than those in the table. Capacitance uncertainties in the table may be compared with total capacitances measured in the cell. Direct air capacitances between the electrodes typically lie in the range 4 to 30 pF for measurements which contribute to the final result while corresponding capacitances for ethanol are in the range 100 to 700 pF. All quoted uncertainties are for a coverage factor of $k=2$, corresponding to approximately 95% confidence level. Uncertainties in capacitance are presented as $\pm \Delta C$ and uncertainties in static permittivity as $\pm \Delta\epsilon_s$. In the final column, pentan-1-ol and ethanediol are generally used to show the effect of the uncertainties in measurements upon 'low' and 'high' permittivity liquids respectively - their static permittivities are approximately 15 and 44 respectively - but other liquids are used for illustration where appropriate.

Table 1. Uncertainty Budget for the Unmodified Cell

Source of Error	Method of Derivation	Uncertainty ($k = 2$) in parameter	Uncertainty ($k = 2$) and Comments
Impedance analyser uncertainties	Estimation and check measurements on traceable capacitors	Various	Total contributions typically: $\Delta\epsilon_s \sim \pm 0.0086$ for pentanol $\Delta\epsilon_s \sim \pm 0.022$ for ethanediol.
Effective series inductance	Measured as 42 nH	± 10 nH	$\Delta\epsilon_s \sim \pm 0.0001$ for pentanol $\Delta\epsilon_s \sim \pm 0.0004$ for ethanediol.
Stray capacitance	Measured as 0.0035 pF	± 0.0035 pF	$\Delta\epsilon_s \sim \pm 0.0058$ for pentanol $\Delta\epsilon_s \sim \pm 0.0166$ for ethanediol.
Air capacitance	Measured and computed	$\pm 0.16\%$ weighted average over all micrometer settings.	Accounts for uncertainty in the attributed air cap. for each liquid cap. $\Delta\epsilon_s \sim \pm 0.026$ for pentanol $\Delta\epsilon_s \sim \pm 0.068$ for ethanediol.
Effective micrometer zero error	Measured and computed	± 0.004 mm	$\Delta\epsilon_s \sim \pm 0.0156$ for pentanol $\Delta\epsilon_s \sim \pm 0.042$ for ethanediol.
Setting the micrometer	Measured	± 0.0004 mm	$\Delta\epsilon_s \sim \pm 0.0116$ for pentanol $\Delta\epsilon_s \sim \pm 0.032$ for ethanediol.
Residual electrode polarisation effect	Extrapolated from lower frequencies: depends on conductivity	Depends on frequency	$\Delta\epsilon_s \sim \pm 0.0048$ for methanol $\Delta\epsilon_s \sim \pm 0.0028$ ethanol. but below ± 0.0002 for other liquids as they have much lower conductivity
Dielectric relaxation	Computation from relaxation parameters	Various	Difference in permittivity at the measurement frequencies and ϵ_s . $\Delta\epsilon_s \sim \pm 0.0068$ for pentanol, all others less
Temperature	Measurement and computation	Typically $\pm 0.2^\circ\text{C}$ * see note	$\Delta\epsilon_s \sim \pm 0.044$ for ethanediol. all others less

* Since the improvement of the cell this is now $\pm 0.1^\circ\text{C}$ between 20 and 30°C , but remains $\pm 0.2^\circ\text{C}$ at the extremes of the temperature coverage, 5 and 50°C .

It will be seen that temperature, electrode spacing errors, and errors in computed air capacitance and stray capacitance dominate the uncertainties. Every attempt has been made in the latest round of measurements to reduce these dominant uncertainties. For example, the recent modifications to the cell have made temperature variation less significant as a major source of error at near ambient temperatures.

Measurement Results

A selection of NPL results is presented in Table 2. The table compares the latest measurements, (a), with previously obtained data, (b) and (c). The latter are limited to 20 - 30°C :

- (a) Recent NPL measurements of static permittivities in the improved admittance cell.
- (b) Static permittivities obtained at NPL [3] in the unmodified cell, 1990 - 1992.
- (c) Static permittivities obtained at NPL [3] by extrapolating microwave permittivity measurements to low frequencies, 1990 - 1992.

Except where otherwise shown, all liquids are at least 99.5% pure ('Analar', 'Aristar' or 'Special for Spectroscopy' grades). Full details and results will be published in the scientific literature.

The table illustrates the high level of agreement that can be obtained from different experimenters and techniques. Where discrepancies exceed combined uncertainties, adequate reasons have been found in some, but not all cases. For example, the extrapolated value for methanol at the top of Column 5 is thought to have been affected by liquid seepage in a microwave cell. Full uncertainty budgets for the extrapolated figures in Column 5 are difficult to estimate and it would be inappropriate to reproduce the estimates and provisos at length here, but this very difficulty does underline the need for direct static permittivity measurements to underpin RF and Microwave dielectric traceability - estimation of uncertainties is more simple for such direct measurements. Four other liquids have been measured in the recent programme of work which are not included in the table: deionised water, 1 centistokes silicone fluid, cyclohexane, and dimethyl sulphoxide.

Table 2 Comparison of Static Permittivities with Previously Measured Values.

All measurements were performed at NPL
Uncertainties are for a coverage factor of $k = 2$.

Liquid	Temp. °C	ϵ_s New Measurements Estimated Uncertainties *	Previously Measured ϵ_s [3]	Previously Measured Extrapolated ϵ_s [3] †
Methanol	5	36.84 ± 0.09		
	20	33.64 ± 0.06	33.65 ± 0.10	34.10 (± 0.05)
	30	31.71 ± 0.06	31.70 ± 0.10	31.76 (± 0.04)
	50	28.22 ± 0.09		
Ethanol	5	27.64 ± 0.07		
	20	25.16 ± 0.04	25.28 ± 0.08	25.30 (± 0.03)
	30	23.65 ± 0.04	23.78 ± 0.08	23.87 (± 0.03)
	50	20.80 ± 0.07		
Propan-1-ol	5	23.36 ± 0.07		
	20	21.15 ± 0.04	21.19 ± 0.08	21.08 (± 0.14)
	30	19.76 ± 0.04	19.79 ± 0.08	19.94 (± 0.08)
	50	17.13 ± 0.07		
Propan-2-ol	5			
	20	Not yet measured	20.23 ± 0.07	20.23 (± 0.13)
	30		18.66 ± 0.07	
	50			
Butan-1-ol	5	20.24 ± 0.07		
	20	18.19 ± 0.04	18.21 ± 0.06**	18.19 (± 0.02)**
	30	16.89 ± 0.04	16.93 ± 0.06**	
	50	14.45 ± 0.07		
Pentan-1-ol	5			
	20	Not yet measured	15.66 ± 0.05	15.64 (± 0.03)
	30		14.49 ± 0.05	
	50			
Ethanediol	5	45.57 ± 0.09		
	20	41.89 ± 0.06	41.95 ± 0.12	41.99 (± 0.18)
	30	39.67 ± 0.06	39.61 ± 0.12	
	50	35.74 ± 0.09		
Acetone	5	22.79 ± 0.07		
	20	21.13 ± 0.04	21.30 ± 0.07	not measured
	30	20.10 ± 0.04	20.14 ± 0.07	
	50	-		

Notes: * The uncertainties in Column 3 are the current best estimates. Studies to finalise the uncertainty budget are still ongoing at the time of writing this paper.

** The purity of the butan-1-ol in 1990-92 was only 99.0%

† The uncertainties in parentheses in the final column are for the goodness of fit to a Debye relaxation only. They do not cover the total uncertainty of the microwave measurements.

Discussion

The three sets of measurements presented in Table 2 provide values of static permittivity with uncertainties that are more than adequate for most practical purposes. However, for provision of traceability and for use as calibration standards, uncertainties of this order are certainly required. One reason for this is that unless the reference and measured liquids are closely matched in permittivity an error of 0.2%, for example, in the permittivity of a calibration liquid can give rise to a much larger error, e.g. 1%, in permittivity measurements dependent upon that calibration. Another reason for providing such accurate values of permittivity is to improve confidence in measurement. Confidence is much enhanced by close agreement of values obtained by a variety of techniques, especially when they are obtained independently by different experimenters, as here.

For those intending to use these tabulated permittivities for calibrating and checking dielectric measurements, a few words of warning must be given. The figures only apply to pure reference liquids. The liquids are easily contaminated and their permittivities change significantly when they are impure. Cells must therefore be

thoroughly cleaned and liquids should be used only once, straight from the bottle, so that they do not absorb moisture from the atmosphere. The temperature must also be controlled and measured to a suitable level of accuracy because their dielectric properties change rapidly with temperature.

These static permittivity determinations are just one part of an NPL project aimed at providing better confidence in RF and microwave dielectric measurements by referencing them to standard data specifically obtained for (and by) RF and microwave metrologists. The body of previously published data on permittivity of reference liquids has failed to do this because it is not always self-consistent [2]. This goal cannot be considered fully achieved until measurements at other laboratories are undertaken for comparison with the NPL values. For this reason NPL is promoting international comparisons of permittivity measurement upon reference liquids.

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References

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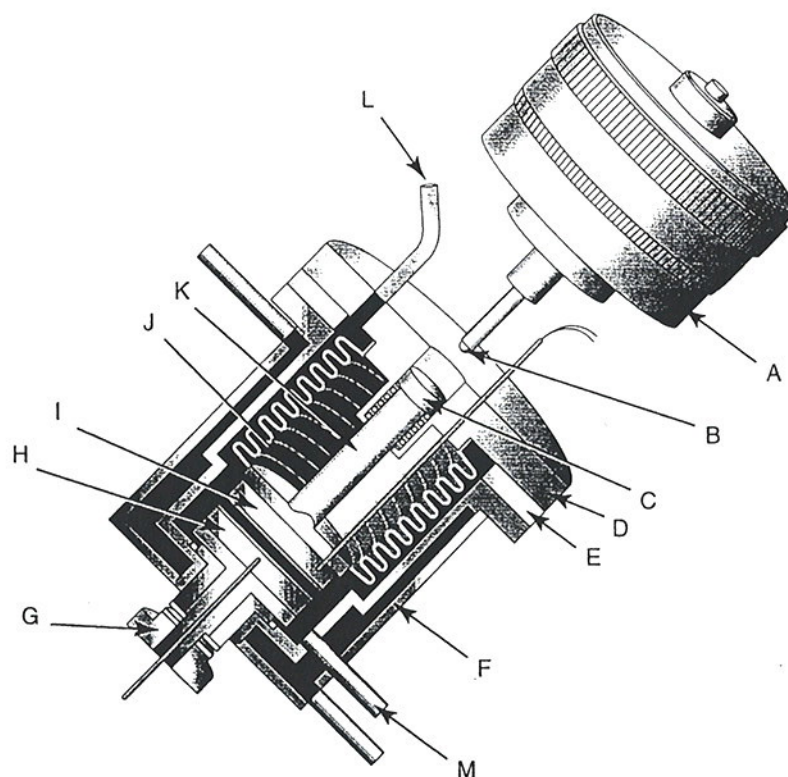


Figure 1. The admittance cell. Key: A: micrometer, B: ball bearing, C: PEEK thermal insulator, D: upper assembly, E: PEEK electrical and thermal insulator, F: screen/shield with internal water duct for temperature control, G: lower electrode contact, H: 'Low' electrode, I: 'High' electrode, J: bellows, K: drive rod for 'High' electrode, L: riser for liquid under test, M: inlet for liquid under test.