Measurements of the Electrical Conductivity of Water

R G Jones

National Physical Laboratory
Teddington
Middlesex TW11 0LW

1. Abstract

The electrical conductivity of water is used in many industries as an indication of the purity of the water. This paper describes a system for the traceable measurement of the conductivity of water in the range 0.01 S/m to 1 S/m. The method is based on the measurement of the resistance of a column of water of accurately known dimensions. There is an electrode polarisation effect and the convention is to extrapolate the conductivity as a function of inverse frequency to find the value at zero inverse frequency. The temperature coefficient of the conductivity is 2 % per Kelvin at 25°C and this limits the uncertainty of the measurement to about ± 0.15 % in the present system.

2. Introduction

This paper describes a system for the traceable measurement of the conductivity of water in the range 0.01 S/m to 1 S/m. The method is based on the measurement of the resistance of a column of water of accurately known dimensions.[1], [2]. There is an electrode polarisation effect and the convention is to extrapolate the conductivity as a function of inverse frequency to find the value at zero inverse frequency, i.e., infinite frequency. [3]

3. Measurement System

Reference liquids for calibration of conductivity meters are made by making solutions of known concentration of potassium chloride in pure water. The procedure here is not to use a reference liquid but to calibrate a conductivity meter by filling both the device under test (DUT) and the reference system using a liquid of approximately known conductivity. Commercially available reference liquids can be used for this purpose. The conductivity of the liquid is then determined using the reference system and the value compared with the reading of the DUT. The method does not require a liquid of known conductivity, only that that the liquid in each measuring system has the same conductivity. This method does not rely on a procedure for preparing a reference liquid of known conductivity or on any knowledge of how the conductivity of the reference liquid changes with time.

The method does require that the two systems are clean and at the same temperature and that the liquid handling system does not contaminate the liquid.

The measurement cell is shown in Figure 1.

The measurement cell consists of two end reservoirs in which the platinum electrodes are placed. These are separated by a removable centre section 100 mm long and 10 mm diameter. The resistance between the electrodes is measured as a function of frequency with, and without, the centre section in place. The difference gives the resistance of the centre section. This value together with a knowledge of the dimensions of the centre section, gives the conductivity of the liquid.

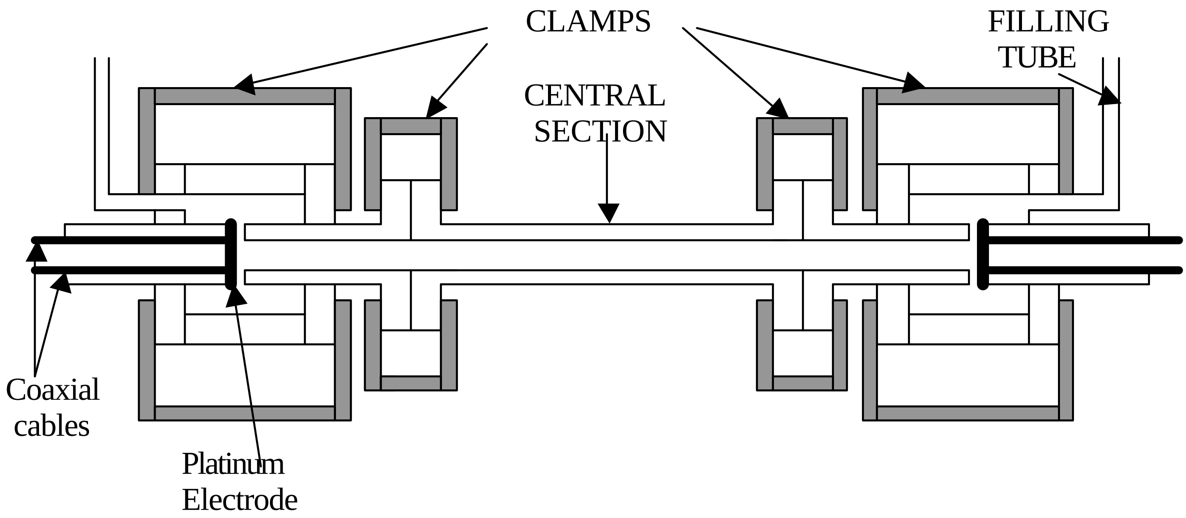

Figure 1, Conductivity cell

The resistance is measured using a commercial four terminal pair impedance bridge. In order to avoid any uncertainty due to additional lengths of cable in series with the electrodes, the coaxial cables are taken up to the back surface of the electrodes and both inner conductors are spot welded onto the back surface.

Where possible the bridge is calibrated using Wilkins type ac-dc resistors.

The dimensions of the centre section were measured by the NPL Engineering Dimensional Measurements Section.

Because the conductivity is so dependent on temperature (2% per kelvin) the cell is placed in a temperature controlled air bath. An oil bath would in principle be better, but the possibility of contamination would be greater and a customer's instrument could not be placed in such a bath.

The temperature is measured using calibrated platinum resistance thermometers (PRT). Two PRTs are used, each placed in a small oil filled container close to the cell. The temperature of the air bath can be varied between 17°C and 30°C. In general most reference liquids are measured at 25°C. As it is not possible to set the air bath temperature to exactly 25°C the measurements are made at three temperatures close to the desired temperature and the value of resistance at the desired temperature obtained by interpolation.

For ionic liquids electrode polarisation takes place at the surface of the electrodes. The effect of this on the measurements is usually catered for by measuring over a range of frequencies (500 Hz to 10 kHz) and plotting a graph of resistance as a function of inverse frequency. The intercept at zero gives the value of the bulk resistance at infinite frequency.

4. Calculation of conductivity

The intercept at zero of graph of resistance against inverse frequency is obtained by linear regression. This is done at three temperatures around 25°C. The linear regression method is also used to fit a line to these data and the value at 25°C obtained using the calculated coefficients. This is done for the configurations with and without the centre section. The difference in the two 25°C values gives the resistance of the centre section at 25 °C.

The conductivity σ is obtained from

$$\sigma = (L/A)R$$

where L and A are the mean length and mean cross-sectional area of the cylinder and R is the resistance calculated as indicated above.

5. Uncertainty calculation

The main uncertainty contributions for one resistance measurement, eg, for centre section out, are listed in Table 1. The uncertainties due to temperature measurement are translated into resistance units using the coefficient of 2 % /K.

Contribution	Value of standard uncertainty in resistance μΩ/Ω
Calibration of resistors	29
Calibration of bridge	30
Measurement of resistance	60
Uncertainty of 1/f intercept	151
Uncertainty due to temperature measurement	328
Uncertainty due to PRT calibration	108
Uncertainty due to estimate of 25°C resistance value	200
Combined standard uncertainty	487

Table 1 Uncertainty calculation for resistance measurement

There is a similar table for the measurement of the resistance of the cell with the centre section in place.

The combined standard uncertainty of the resistance of the centre section assuming worst case correlation is 695 μΩ/Ω

Table 2 gives the uncertainties for the dimensional measurements

Contribution	Standard uncertainty μm/m
Length	154
area	20

Table 2 Uncertainty contributions for dimensional measurements

The final uncertainty expressed for a coverage factor of 2 is ± 1 420 μS/S

The main contribution to the uncertainty comes from the large (2% / K) temperature dependence of the conductivity of the solution. The uncertainty in measuring the temperature of the cell in a large air bath is due to the temperature gradients in the bath.

5. Conclusions

A reference system for the measurement of the conductivity of water has been constructed. Measurements can be made with an uncertainty of 0.15 %. The system can be used for the calibration of conductivity meters.

Acknowledgement
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6. References

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