

## DIELECTRIC SPECTROSCOPY AS A TOOL FOR FOOD PROCESS CONTROL

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### Background

Food safety, quality and stability are major challenges for the food industry. Three of the parameters that have to be controlled are salt content, water content and water state. Dielectric properties are closely correlated with water content and state in a material [1, 2, 3, 4] and also with conductivity associated to salt content for instance. It has long been recognised that water activity ( $a_w$ ) in food products depends on both bound and free water. Hence it is possible to access the water activity, water content, and salt content of a product via its dielectric properties.

In particular, dielectric relaxation spectroscopy determines the response of molecular motion of polar molecules in the sample to a weak external alternating electric field. As the electric field frequency is increased, it reaches a frequency called the relaxation frequency ( $f_R$ ) when the polar molecule can no longer rotate with the electric field. Dielectric properties change markedly around this relaxation frequency.

### Objectives

Measurement methods and associated sensors already exist to determine these three parameters [5, 6], but often are long and not adapted for *in situ* measurements.

The purpose of this work was to show the feasibility of a microwave sensor, which is potentially very fast and could allow in-line measurements. We present here some results concerning water content, salt content and water activity of gelatine samples.

### Methods

Forty-four samples were prepared. They were made up with a commercial animal gelatine powder (PS 60 Bloom, from SKW Biosystems SAS, Angoulême, France), de-ionised water and NaCl (99.5%, from ACROS) to depress  $a_w$ . All the components were mixed at 40°C and heated from 40 to 80°C in about one hour. The samples were then poured into tubes and left to cool at 18°C for one day.

Water content ranged from 0.9 to 10 kg per kg of dry matter, salt content from 0 to 0.12 kg per kg of dry matter and  $a_w$  ranged from 0.942 to 1. This  $a_w$  range covers water activities in fresh produce and particularly in meat products, where bacterial growth is particularly relevant.

The coaxial line reflection method [7] was used for dielectric measurements. The experimental system, shown schematically in Figure 1, consists of an open-ended coaxial line probe HP 87090 and an HP 8753 automatic network analyser (Hewlett Packard, CA, USA) equipped with the HP85047A S-parameter test set. All the instrumentation was computer-controlled via a GPIB (General Purpose Interface Bus).

The coaxial line reflecting probe is a coaxial line with a flat end for contact between the sample and the probe. An electromagnetic wave is emitted at the probe-sample interface and the network analyser measures the vectorial reflecting coefficient  $\Gamma$  at the interface. With known probe geometry (and so the capacitance  $C_0$  (intrinsic to the probe) and  $C_f$  (capacitance in the sample, external to the probe)), software

computes the complex permittivity ( $\epsilon^* = \epsilon' + j\epsilon''$  with  $j = \sqrt{-1}$ ) of the sample as described below:

$$\epsilon^* = \frac{1 - \Gamma}{2\pi f C_0 Z_0 (1 - \Gamma)} - \frac{C_f}{C_0} \quad (1)$$

where  $f$  is the frequency and  $Z_0$  the characteristic impedance of the coaxial line.

This probe is very useful and fast (a few seconds per measurement) but also presents some difficulties: presence of air if contact between sample and probe is not carefully controlled, variations in pressure and problems due to poor homogeneity in samples. Accuracy for permittivity measurement is about 5%.

The dielectric permittivity measured at lower frequencies (below 100 kHz) can be seriously perturbed by electrode polarisation effects [8], but in our frequency range this was not significant.

Water activity measurements were done with an industrial device, the *aw Sprint* from Novosina, Switzerland. It consists of a fluid-tight low volume cell in which the sample is placed, and a humidity

sensor. If the sample is left in the cell long enough, it reaches an equilibrium with the air in the cell. The humidity sensor measures water content in air, which gives water activity in the sample. It operates from 0 to 50°C and can measure water activity from 0.06 to 1. The *aw Sprint* is a fully automatic computer-controlled device.

Water content of each sample is determined by oven drying at 106°C for 24 hours. Salt content is obtained by weighing of salt, water and gelatine on a laboratory balance ( $\pm 0.1$  mg).

### Results and discussion

Results presented here show relation between: water content and real permittivity at 6 GHz, salt content and imaginary permittivity at low frequency, and water activity and relaxation frequency.

Figure 2 shows the logarithmic relation between the real part of permittivity at 6 GHz and the water content, for two different salt contents. As well known, dielectric permittivity increases with water content. We choose the 6 GHz permittivity in order to be far enough from the low frequency where conduction phenomenon predominates.

On the other hand, this conduction phenomenon is useful to control salt content in the samples (Figure 3). Low frequency imaginary part of permittivity is proportional to salt content. Imaginary part corresponds to dielectric losses in the material, and the presence of ionic compounds (here:  $\text{Na}^+$  and  $\text{Cl}^-$ ) leads to losses by conduction. This conduction only concerns low frequency because at upper frequency ions can no longer translate in the material during a period of the electric field.

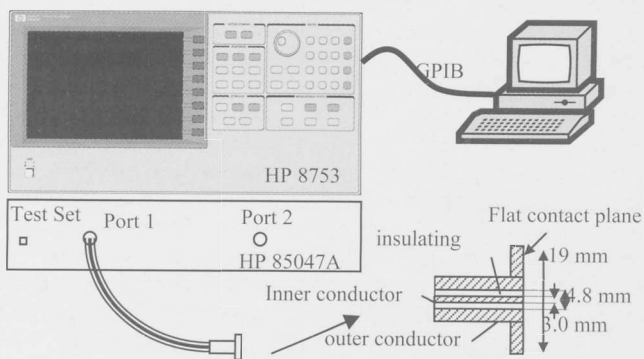


Figure 1: dielectric measurements experimental device.

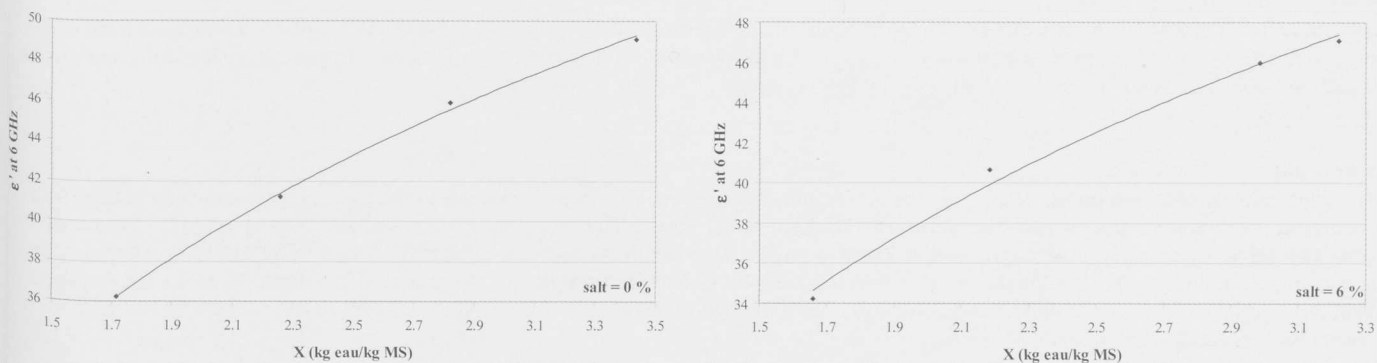


Figure 2: real permittivity at 6 GHz versus water content for 2 different salt contents.

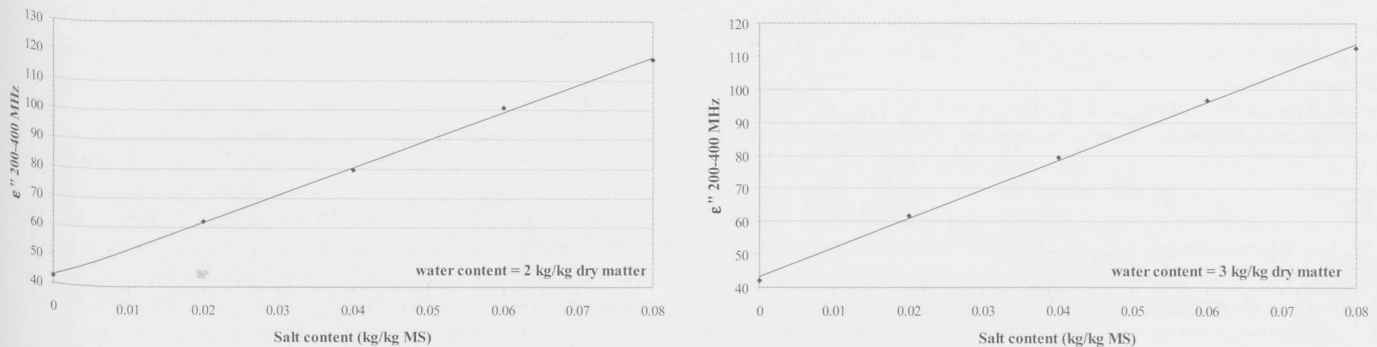


Figure 3: imaginary permittivity at low frequency versus salt content for 2 different water contents.

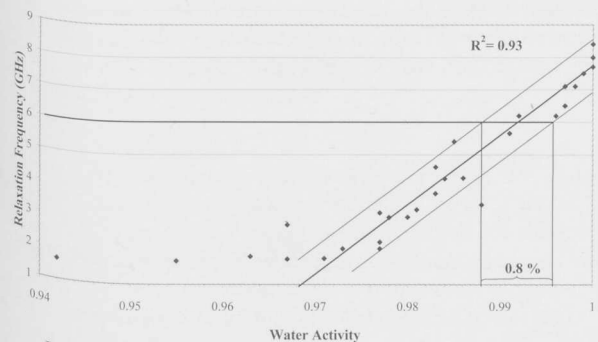


Figure 4: relaxation frequency versus water activity.

Figure 4 gives the relaxation frequency of our samples versus water activity. To extract this frequency experimental data are fitted with the Debye relation:

$$\epsilon'(\omega) = \epsilon'_\infty + \frac{\epsilon'_s - \epsilon'_\infty}{1 + \omega^2 \tau^2} \quad \text{and} \quad \epsilon''(\omega) = \frac{(\epsilon'_s - \epsilon'_\infty) \omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

where  $\omega$  is the angular frequency  $\epsilon'_s$  the static permittivity (at low frequencies),  $\epsilon'_\infty$  the high frequency permittivity and  $\tau = 1/f_R$ . This relation is the theoretical variation of permittivity with frequency for a monomolecular material.

When water activity increases, water molecules are less tightly bound and so can easily rotate, and the relaxation frequency then increases as shown in Figure 4. The curve has two parts: a linear increase for  $a_w$  above 0.97, and a threshold below it. This threshold is easily explained by the contribution of conductivity phenomena at low frequencies. For relaxation frequencies below 2 GHz, the maximum in  $\epsilon''$  curve is lost in the  $\epsilon'$  increase due to conductivity.

Obviously, it is then difficult to fit the experimental results with the Debye relation at low frequency. Results show that for  $a_w$  below 0.9, the relaxation frequency is in our frequency range ( $f_R < 6$  GHz). In this range, he frequency relaxation parameter can predict  $a_w$  with a 0.8 % error.

To improve this experimental method, which allows water and salt content measurement and  $a_w$  quantification, and adapt it for real materials, we need to make more sample measurements, on different kinds of model materials, but also on food products. Although much work remains to be done to obtain an operational experimental method, both industrial applications and the performance of research tools stand to benefit.

**Pertinent literature**

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