

Dielectric spectroscopy of sugar and ethanol solutions in water for monitoring alcoholic fermentation processes

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Abstract. The dielectric properties of water solutions of ethanol and sugar are investigated in the microwave region, with the objective of setting up a method for the quality control of the fermentation process of alcoholic beverages. Alcoholic fermentation is the process by which carbohydrates, in particular sugar, are converted by the yeast into alcohol. During that process several other by-product compounds are produced, including a significant amount of carbon dioxide. The fermentation stage is of fundamental importance in the production of alcoholic beverages, because some of the by-products components have a considerable effect on the flavour, aroma, and other characteristic properties of the beverages. The on-line monitoring of the fermentation process can thus be very useful for controlling the timing and the development of the process, in order to early correct it if deviations from "normality" occur. Dielectric spectroscopy is shown to be suitable for such a task, being it able to discriminate between the initial water–sugar mixture and the final water–alcohol solution and making it possible to detect the production of carbon dioxide during fermentation. A case-study, consisting in the monitoring of the primary fermentation of beer by dielectric spectroscopy, is presented and discussed.

Key Words: Dielectric spectroscopy, dielectric properties, alcoholic fermentation, alcohol solutions, sugar solutions, food diagnostics

1. Introduction

The core of fermentation consists in converting sugars, such as glucose (C₆H₁₂O₆) or sucrose (C₁₂H₂₂O₁₁), to ethyl alcohol (CH₃CH₂OH) and carbon dioxide gas (CO₂). The reactions within the yeast, to accomplish this, are very complex. A few considerations can help in understanding the complexity of the dynamics of the fermentation process: if sucrose – a composite of α -glucose and fructose joined by a glycosidic bond – is the sugar involved in the reaction, it is first hydrolyzed into glucose and fructose, and subsequently glucose is utilised at about twice the rate of fructose [D'Amore 1989], up to a total or partial consumption of the two sugars, depending on the chemical and physical conditions of the solution.

However, the process can be schematically represented as follows, when the reaction involves only glucose:

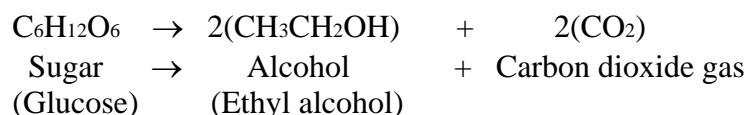


Figure 1: Outline of the alcoholic fermentation process

The production of beer, for example, essentially involves four steps: (1) primary fermentation, (2) conditioning, (3) filtration, (4) carbonation. Step no. (1), involving the conversion of carbohydrates into alcohol, requires 6 – 10 days depending on the yeast type and on environmental conditions. Step no. (2) consists in maturation, clarification and chill-proofing, i.e. in removing proteins or poly-phenols and in

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improving the physical stability of beer. Step no. (3), usually employing centrifugation and powder filters, is required to remove suspended particles and sediments. Step (4), finally, is accomplished by a secondary fermentation and/or CO₂ addition, to obtain the desired carbon dioxide concentration. Other alcoholic beverages have rather different, and sometimes more complex, preparation procedures but, in every case, the main fermentation process involves a sugar-to-alcohol conversion like that shown in Figure 1.

With reference to beer fermentation, steps (1) and (4) can be monitored by means of dielectric spectroscopy, looking at the sugar/alcohol conversion (in primary fermentation) and estimating the CO₂ content (both in primary and secondary fermentation).

The dielectric constant of an aqueous solution such as the liquid portion of mash (also called *wort*) strongly depends on the volume fraction of water and of the other constituents. Before the fermentation process, the wort is a complex mixture of water, carbohydrates (mainly sugars), yeasts and more. After alcoholic fermentation it contains water, alcohol, carbon dioxide and other chemical compounds. During the process the main changes consist in a partial or full conversion of sugar into alcohol and in a substantial production of carbon dioxide. Other compounds are also produced as a consequence of the interactions between yeast and bacteria in the mash: the relative amount of such compounds strongly depends on the characteristics of the environment (temperature, alcohol and CO₂ content, etc.) and it has a considerable effect on the characteristic properties of a beverage, such as its flavour [Fleet, 2003].

During the chemical transformation of a beverage, its dielectric constant is a function of the permittivity of the various constituents and of their volume fractions. Simplifying the situation, the chemical process of Figure 1 transforms an aqueous solution containing sugar in a solution of alcohol in water. It is well known that the dielectric constant of aqueous solutions is very sensitive to the water content up to microwave frequencies, i.e. below water relaxation, suggesting the suitability of microwave techniques for distinguishing between the initial solution (essentially water+sugar) and the final solution (water+sugar+alcohol). Microwave dielectric spectroscopy will be demonstrated to allow setting up a non-polluting, real-time, in-flow system for monitoring the production of beer. The extension to other alcoholic beverages, in particular to wine, appears rather feasible.

2. Materials and Methods

2.1 Dielectric properties of alcohol solutions

Alcohols are polar liquids. An aqueous solution of alcohol can not therefore be rigorously treated as a binary mixture, because the two molecular species (alcohol and water) strongly interact. For small solute concentrations, it has been shown [Hasted, 1973] that the solution can be roughly treated as a mixture, having a permittivity ϵ_m which depends on alcohol concentration c (usually expressed in moles/liter, i.e. denoting the solution molarity) as follows:

$$\epsilon_m = \epsilon_w - \delta_a c \quad (1)$$

where ϵ_w is the permittivity of water and δ_a is the dielectric decrement due to the polarization of alcohol molecules, that can be computed according to the various mixture theories and formulas [Sihvola, 1999]. For increasing concentrations of the polar solute, equation (1) is no longer a reasonable approximation as the mixing of the two polar components becomes more and more intimate and the hydrogen bond interactions make the mixture approach hardly applicable. Some experimental results concerning the dielectric properties of aqueous alcohol solutions have been published in the last decade, proposing the Cole-Cole equation (2) [Smith, 1998] or the Cole-Davidson equation (3) [Bao, 1996] to describe the observed dispersion of the complex permittivity ϵ^* .

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (2)$$

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta} \quad (3)$$

with the well known meaning of the various parameters involved (ε_∞ and ε_s are the high-frequency and low-frequency limits, respectively; τ is a relaxation time; α and β are empirical parameters).

Beverages like beer and wine exhibit an ethanol content ranging from 4 to 16 % in volume. The dielectric properties at microwaves of water solutions of ethanol in such a range of concentrations have been investigated by means of a measuring system consisting in a vector network analyzer Agilent E8364B (10 MHz – 50 GHz) and a dielectric probe kit Agilent 85070E. The dielectric properties of ethanol solutions with volume concentrations of 4, 6, 8, 10, 12, 15 and 20 % have been investigated in the frequency range 200 MHz – 20 GHz. The above concentrations are "by volume of the solution", as it is usually defined for beer and wine. In terms of molar concentration, therefore, they span a range between 0.7 and 3.4 mol/l.

As an example, Table 1 reports the complex permittivity of solutions of ethanol in water, having a volume alcohol content of 4%, 10% and 15% at four frequencies, measured at 22 °C. Those solutions are compared to deionised water at 20 °C, in the same Table I. Water dielectric properties are computed according to the Cole-Cole equation, with parameters [Hasted, 1973]: $\varepsilon_s = 80.1$, $\varepsilon_\infty = 4.23$, $\tau = 9.3 \times 10^{-12}$ s, $\alpha = 0.013$.

Frequency (GHz)	Ethanol 4%		Ethanol 10%		Ethanol 15%		Water	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
0.5	77.9	2.4	74.9	2.7	72.3	3.2	80.0	2.2
1	77.7	4.7	74.6	5.3	71.9	6.3	79.9	4.4
10	55.9	33.6	48.8	33.9	40.0	33.8	61.1	32.7
20	31.3	34.3	25.0	31.5	19.4	26.9	36.9	37.3

Table 1: Permittivity of aqueous alcohol solutions at 22 °C compared to water permittivity

Table 1 shows that a solution of ethanol in water is easily distinguishable from plain water by measuring either its dielectric constant ε' and/or its loss factor ε'' .

Figure 2 and 3 respectively show the spectra of ε' and ε'' for ethanol solutions with volume concentrations c ranging between 4 and 20 %. The curves are labelled from 1 to 7, in order of increasing concentration. Both parameters depend on the alcohol volume fraction almost linearly, at least for frequencies below 10 GHz. Above such a value, ε'' is no longer linear with c because of the different relaxation frequency of the solutions.

The dependence of ε' and ε'' on the ethanol volume concentration $c\%$ (% by vol.) at 2 GHz is shown in Figure 4, (a) and (b) respectively. It appears that a simple linear relation like (1) holds both for real and imaginary part of permittivity. The dielectric constant of ethanol solutions, as obtained by a linear fitting on experimental data, is very well described by the following:

$$\varepsilon' = 79.6 - 0.633 c\% \quad (4)$$

with an explained variance greater than 99%. Converting $c\%$ in the molar concentration c , by considering the molar mass and the density of ethanol (46.07 g and 0.789 g/cm³, respectively), the slope coefficient in (4) becomes 3.7 in rather good agreement with dielectric decrement values reported by other authors [Hasted, 1973]. Such a linear dependence is rather surprising, as a 20% by vol. solution (the higher one) is far to be a dilute one, as it corresponds to about 3.4 mol/l.

Also the dielectric loss factor appears to be linearly related to the volume concentration up to 20%, although the variance explained by the model is lower (97%). The fitting result is summarized by (5), this time expressing a "dielectric increment" law, as losses increase with increasing ethanol concentration.

$$\varepsilon'' = 8.35 + 0.245 c \quad (5)$$

Dielectric spectroscopy of ethanol and sugar aqueous solutions

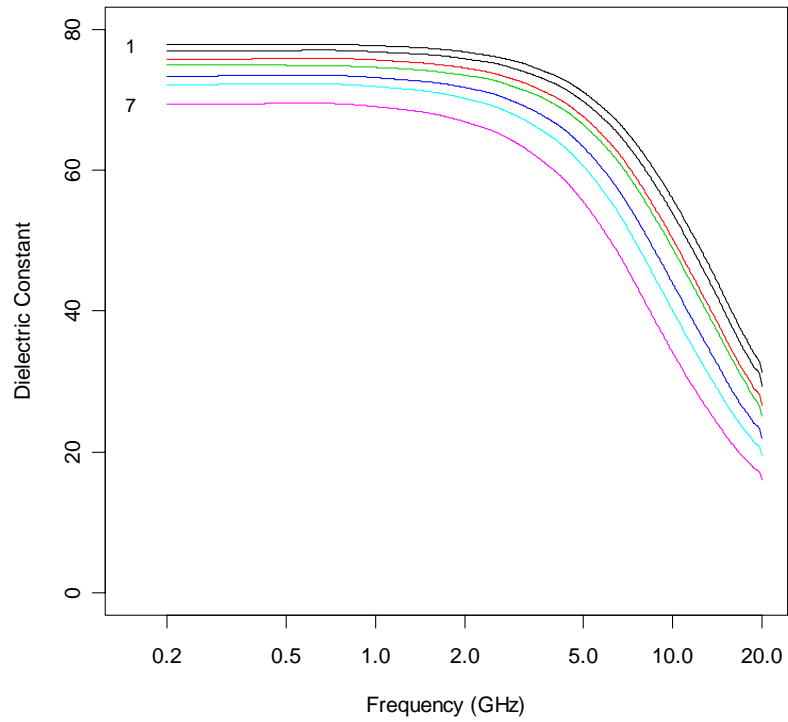


Figure 2: Dielectric constant of water-ethanol solutions at alcohol concentrations ranging from 4% to 20%, at 22 °C

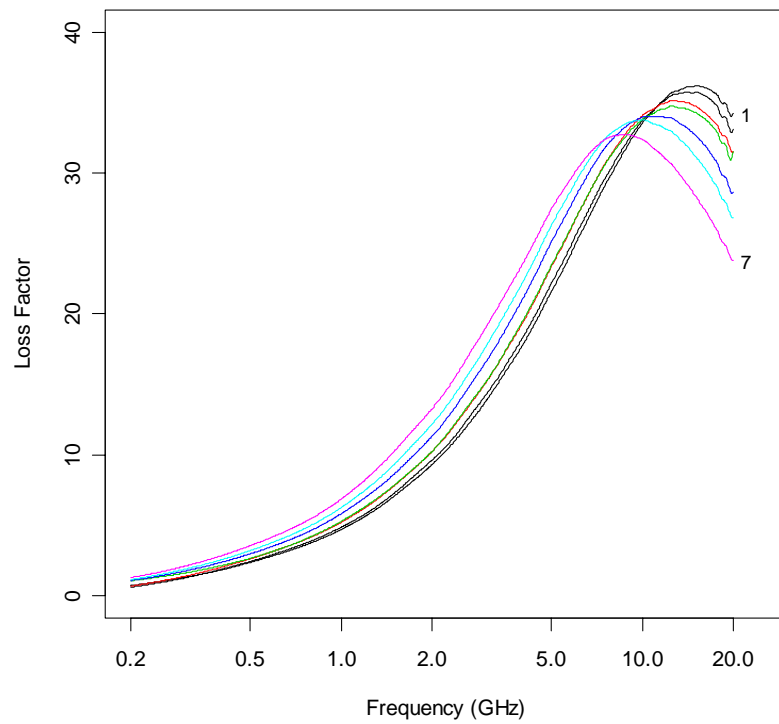


Figure 3: Loss factor of water-ethanol solutions at alcohol concentrations ranging from 4% to 20%, at 22 °C

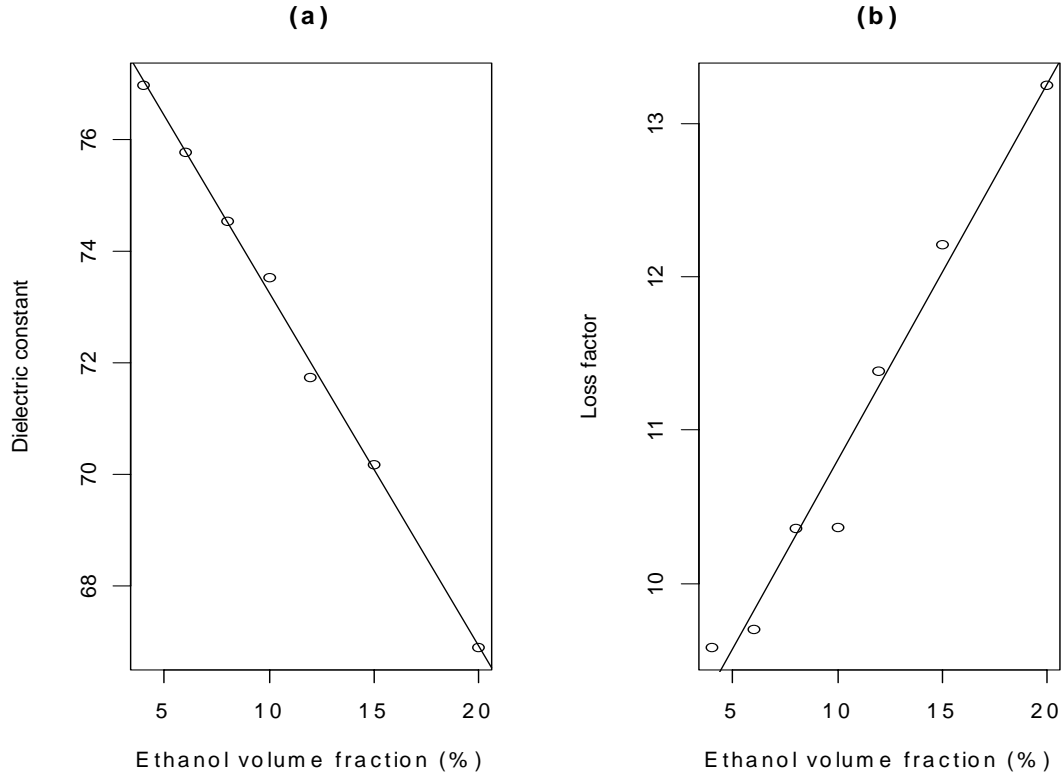


Figure 4: Dependence of the dielectric properties at 2 GHz of water-ethanol solutions on alcohol concentration

2.2 Dielectric properties of sugar solutions

Literature data concerning the dielectric properties of sugar solutions in water, as a function of sugar concentration and frequency, are rather poor. An investigation on the dielectric spectra of aqueous solutions of mono and disaccharides has been recently published [Fuchs, 2002], for a few different molar concentrations and referring to glucose, fructose, maltose and sucrose. The work just cited reports about measurements on sugar solutions between 0.1 and 100 GHz and explains the experimental data in terms of a Cole-Cole spectral function like (2) for molar concentrations up to 1 mol/l and by means of a Cole-Cole function with an additive Debye term for higher concentrations.

The dielectric properties of sugar solutions in water have been measured in the range 200 MHz – 20 GHz, using the system referred to in the previous section. The investigation concerns solutions of sucrose in water having the following concentrations (in grams per liter of solvent): 10, 30, 50, 80, 100, 150 and 300 g/l. Table 2 summarizes the results obtained at four frequencies (0.5, 1, 10 and 20 GHz) for sugar concentrations of 50 g/l, 100 g/l and 150 g/l. In terms of molality, i.e the number moles per kg of solvent, the above concentrations range from 0.03 to about 0.9.

Frequency (GHz)	$c_w = 50$ g/l		$c_w = 100$ g/l		$c_w = 150$ g/l		Water	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
0.5	78.5	2.4	77.3	2.8	75.2	3.1	80.0	2.2
1	78.1	4.6	76.7	5.1	74.4	5.7	79.9	4.4
10	58.5	31.1	55.7	30.6	52.3	30.8	61.1	32.7
20	36.3	35.0	34.0	33.5	30.4	30.7	36.9	37.3

Table 2: Permittivity of aqueous sugar solutions at 22 °C

Figures 5 and 6 respectively show the frequency behaviour of the real and imaginary part of permittivity for sucrose solutions in the whole range of concentrations investigated. Far from relaxation of water, it appears

that the relative dielectric constant decreases as sugar concentration increases, while the loss factor increases. Close to relaxation, the loss factor does not appear to be a suitable parameter for estimating the sugar content.

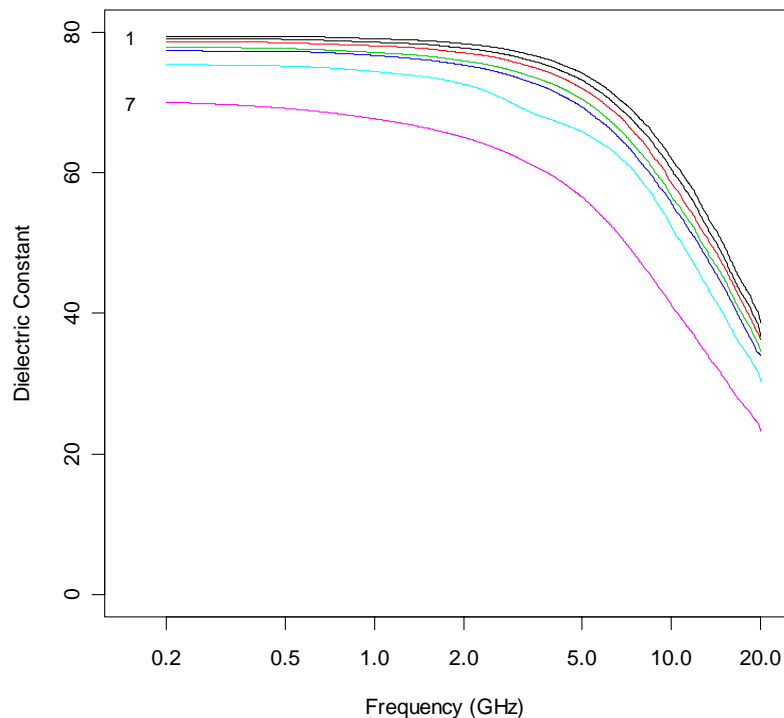


Figure 5: Dielectric constant vs. frequency of sugar solutions in water at 22 °C

The curves in Figure 5 and 6 are labelled from 1 to 7, for concentrations increasing from 10 g/l to 300 g/l. The large range of concentrations is such that a simple linear relation such as (1) is no longer valid as the solution molality increases, say, above 0.3. Figure 7 shows two rather different slopes in the linear fitting of the experimental data, respectively for concentration below and above such a value, corresponding to 100 g/l. The solid lines represent the linear fitting in the lower range of sucrose concentrations, while the dotted ones refer to the higher range.

Dielectric spectroscopy of ethanol and sugar aqueous solutions

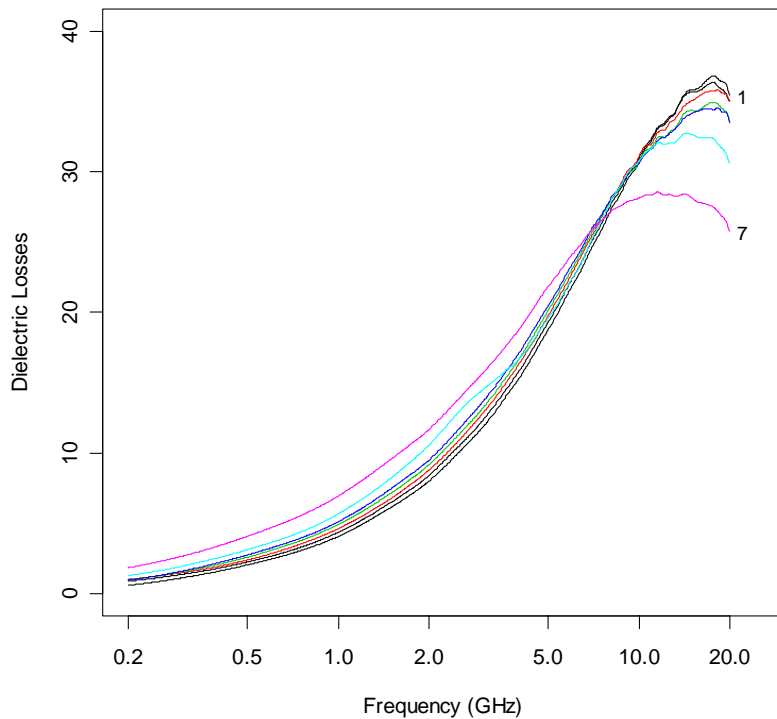


Figure 6: Loss factor vs. frequency of sugar solutions in water at 22 °C

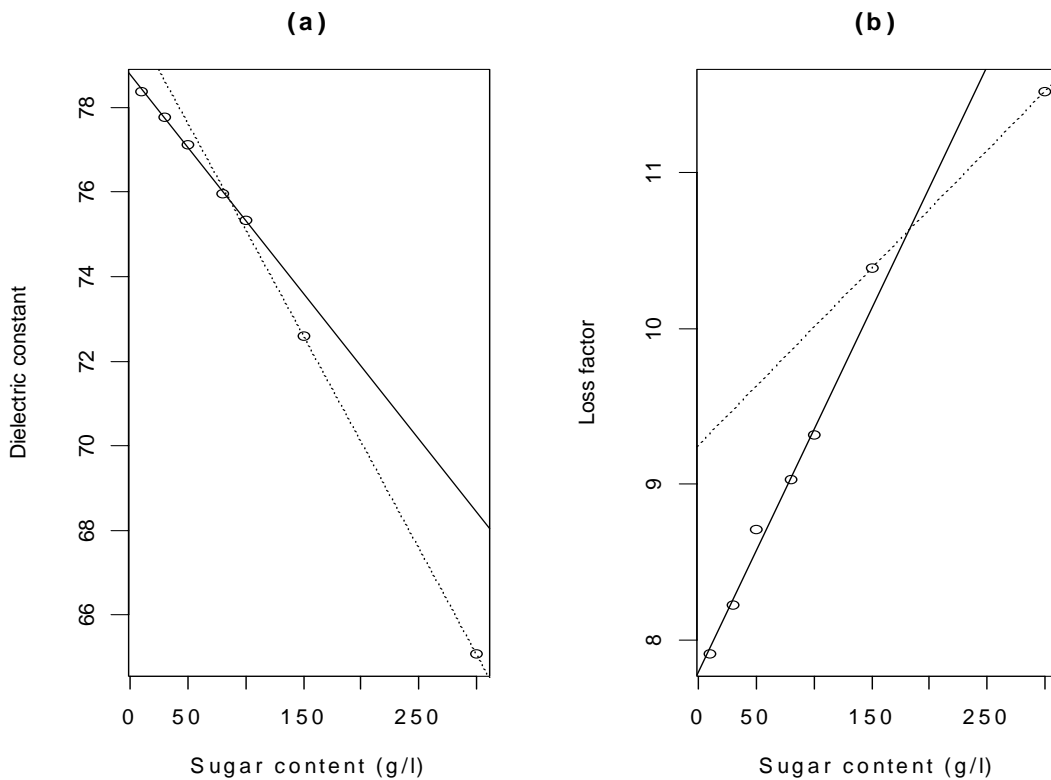


Figure 7: Dependence of the dielectric properties at 2 GHz of water-sugar solutions on sugar content

It will be shown later that in making an "average" beer, a solution having approximately 100 g/l of sucrose is converted into one with ethanol 4% by vol. Figure 8 shows the frequency dependence of the difference between the initial dielectric properties (sugar solution) and the final ones (alcohol solution). A frequency of about 10 GHz appears to be the limit for setting up a monitoring system for such a beverage, based on both dielectric constant and losses. Indeed, above 10 GHz the "contrast" in the loss factor dies off rapidly. A frequency region between 1 and 3 GHz can be a reasonable compromise between sensitivity and cost, in the perspective of setting up a device usable in beer and wine factory too.

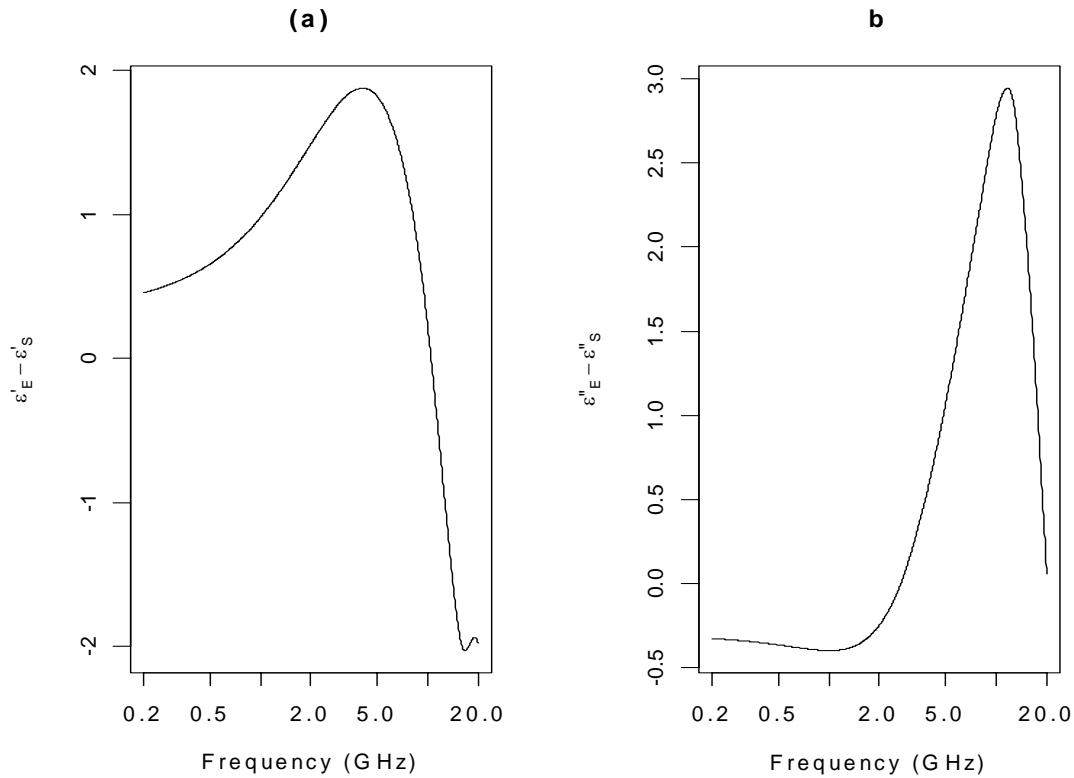


Figure 8: Frequency dependence of the difference in dielectric properties of alcohol (4%) and sugar (100 g/l) solutions

The same conclusions could be drawn directly comparing the Cole-Cole plots for an alcohol solution (4% by vol.) and a solution of sugar (100 g/l) in water as in Figure 9, where the solid line refers to ethanol and the dotted one to sucrose. A marked difference happens to exist, at least in the middle frequency range, among the dielectric properties of the two solutions, suggesting the feasibility of monitoring beer fermentation by dielectric spectroscopy.

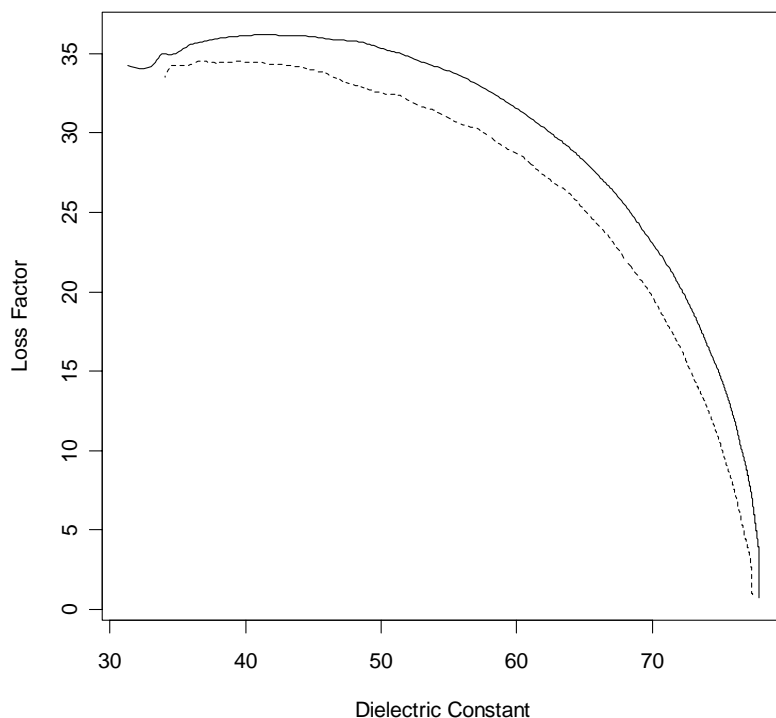


Figure 9: Cole-Cole plots of alcohol (4%) and sugar (100 g/l) solutions

3 Application: dielectric monitoring of beer fermentation

The conclusions of the previous section suggest the possibility of setting up a system for monitoring alcoholic fermentation, based on dielectric spectroscopy in the microwave band.

A prototype of a microwave dielectric spectroscopy system for monitoring beer fermentation has actually been set up. The system operates in the frequency range 0.2 – 3 GHz, and it consists of a Vector Network Analyzer (HP 8753C) with two "twin" miniature open-coaxial probes connected to two ports of the instrument. The miniature probes have been obtained by a semi-rigid coaxial cable Wiltron K 120 having the following characteristics: central conductor diameter 0.81 mm; external diameter 2.4 mm; dielectric: microporous Teflon; upper frequency: 65 GHz with K-connector (SMA 3.5 compatible).

The dielectric monitoring technique has been tested on an "average" beer, i.e. one containing 4–5 per cent of ethanol. In the experiment described in the following, beer has been prepared starting from a commercially processed liquid extract which, according to the developer, contains 20% by weight of water, and 80% of solid material. For 100 g of liquid extract, about 60 g can be estimated to be some form of soluble sugar. The recipes requires adding 1.0 kg of sucrose to 1.5 kg of liquid extract, for a total content of sugar that can be quantified in 1.9 kg. The sugar concentration is estimated to be between 80 and 100 grams per liter of solvent.

Figure 10 shows a sketch of the measurement setup. One of the probes is inserted into a home-brew fermenter via a glass vessel that prevents beer to wet the probe connector and cable and, in the meanwhile, reduces contamination risks. The other probe is inserted in a flask containing plain water, in order to supply a reference and to check the calibration of the whole system. Both probes can be shaken before or during measurement by means of two stirrers. Stirring is fully controllable through the parallel port of a PC controlling the monitoring system, by means of a home-made interface. A thermocouple thermometer allows to record the temperature inside the flask or on the external surface of the fermenter.

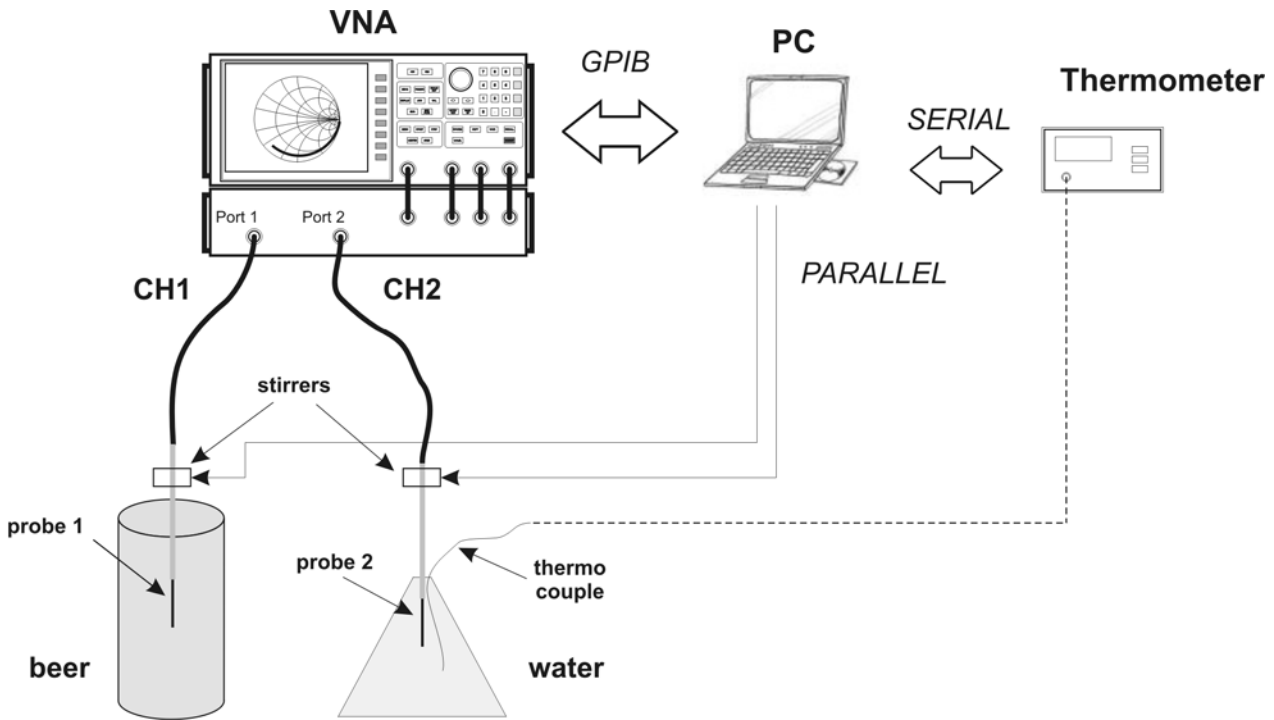


Figure 10: Setup of the microwave dielectric monitoring system

The principle of the measurement is the following. Before brewing, the mash is a complex mixture of water, carbohydrates, sugars, yeasts and more. At the end of the brewing process, beer contains water, alcohol, carbon dioxide and other chemical compounds. During the process the main changes consists in a partial or full conversion of sugar into alcohol and in a substantial production of carbon dioxide. In all those phases, the dielectric constant of the mixture is a function of the individual permittivities of the constituents and of their relative volumes, as shown in the previous sections. The relevant presence of carbon dioxide is expected to be a confounding factor for the dielectric measurement, as the formation of gas bubbles on the surface of the probe would heavily affect the measurement. We will show in the following how this potential problem can be exploited for our advantage.

The setup of figure 10 has been used for monitoring the primary fermentation of a moderately alcoholic beer (4 % nominal). The beer has been prepared starting from a Dry Lager malt syrup, with 1 kg of sugar added. The malt amount was 1.5 kg per 23 liters of final product. The objectives of the dielectric measurement are two: (1) to detect how the dielectric properties of the beer change with time, as a consequence of the conversion of sugar into alcohol; (2) to detect the production of carbon dioxide during fermentation. Both objectives should help in deciding if fermentation is going on regularly or, instead, some kind of manual intervention is needed (temperature adjustment, sugar addition and so on).

Complex permittivity was measured both in a flask containing plain water and in the fermenter. Four measurements were recorded every 10 minutes: two (in the flask and in the fermenter) without stirring, but having shaken the probes 2 seconds before the measurement, and two with continuous shaking.

Figure 11 compares the measured dielectric decrement (i.e the difference between the dielectric constant of beer and that of water) at 2 GHz, during the fermentation process. The control measurement in water is used to take into account systematic errors due to calibration changes simultaneously occurring on both channels, or to correct for permittivity variations due to changes in the ambient temperature. Figure 11 refers to measurements respectively without (on the left) and with (on the right) continuous stirring.

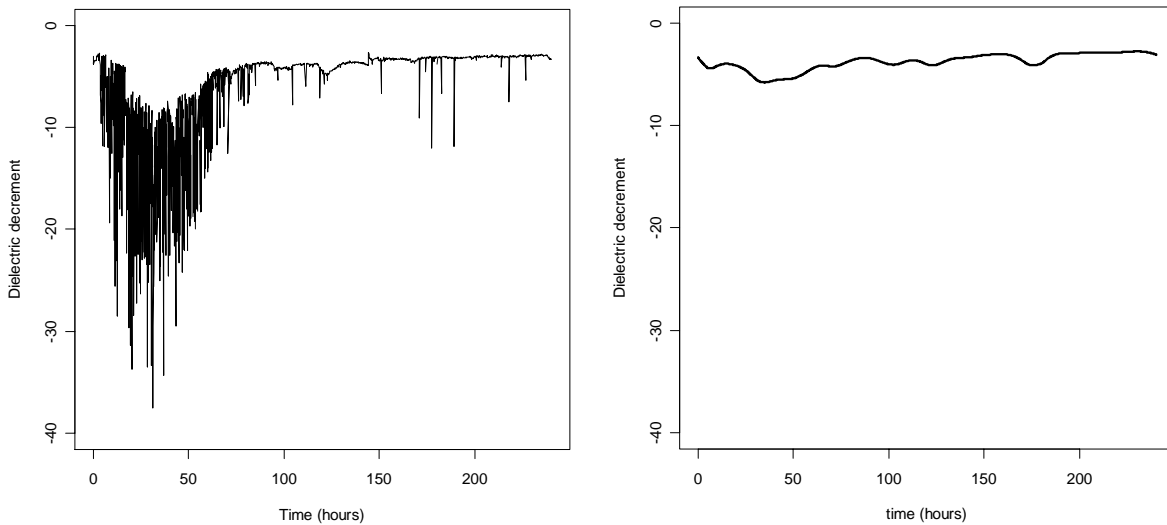


Figure 11: Measured dielectric decrement at 2 GHz, without (left) and with (right) continuous stirring

The two figures have intentionally the same scale to highlight how the stirring affects the measurement. The graph on the left clearly shows the effect of the production of carbon dioxide on the dielectric measurement, due to the deposition of "bubbles" over the sensor surface. After a certain time (about 100 hours) continuously-shaken and not-shaken measurements coincides, suggesting the end of the "explosive" production of carbon dioxide in primary fermentation. Results like those presented in figure 11 have been obtained in the whole investigated frequency range.

Considering the average dielectric decrement $\Delta\epsilon_m$ in the first 4-5 hours (i.e. before the CO_2 production begins) and that, $\Delta\epsilon_b$, in the last 5 hours of the experiment (at the end of brewing), the difference between "beer" and "mash" at 2 GHz is about 1, in perfect agreement with the prevision of Figure 8 at the same frequency. The variation in the dielectric loss factor is rather small, as predicted, making it a less-robust indicator of the fermentation process. A widening of the frequency range up to 5 – 6 GHz would be quite useful, as a consequence of the results of sections 2.1 and 2.2, confirmed by beer measurements in the range 200 MHz – 3 GHz, as it would allow to exploit the whole information contained in the electric permittivity.

Figure 12 shows the time behaviour of the dielectric constant of the mash/beer fluid, corrected for temperature and/or calibration changes detected by measuring the water reference. The measurements have been smoothed by means of a cubic spline to filter out the "spurious" fast time variations. The expected increase in dielectric constant, between the final and initial conditions, is clearly shown, along with a permittivity reduction during CO_2 production. This last is considered to be a real effect, more than an artifact, as during the CO_2 phase the mixture is actually a four-component one: water, sugar, alcohol and carbon dioxide, this last having an almost unitary dielectric constant.

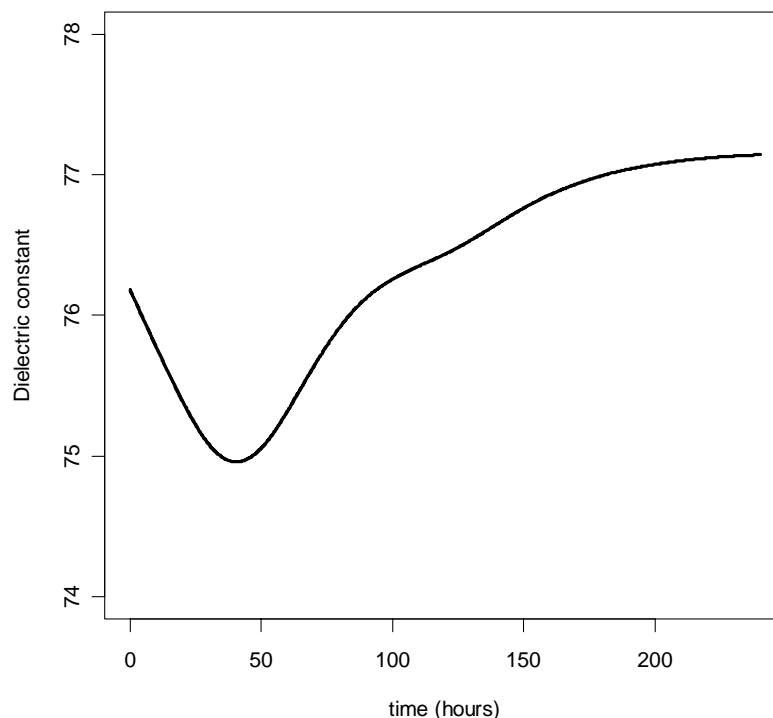


Figure 12: Smoothed time behaviour of the dielectric constant of the mash/beer fluid at at 2 GHz, during fermentation

4. Conclusions

The dielectric characteristics of water solutions of ethanol and sucrose have been investigated in the microwave range between 200 MHz and 20 GHz. It has been shown that dielectric constant is the eligible parameter for discriminating among aqueous solutions with different alcohol or sugar concentrations at microwave frequencies below 3 GHz, while the exploitation of both the real and imaginary part of permittivity would require to resort to a more expensive wider-band system.

Dielectric spectroscopy has been shown to allow a continuous monitoring of beer fermentation, making it possible to follow the production of CO₂ during the process and to detect the conversion of sugar into alcohol. The peculiar characteristics of dielectric spectroscopy, in particular its reliability, low-invasivity and ease of operation, make it a promising method for the monitoring and quality control of the fermentation process of alcoholic beverages, like beer, wine and more.

Acknowledgements

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