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Quantification of free and bound water in selected materials using dielectric and thermo-coulometric measurement methods

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Abstract

Broadband electromagnetic characterization offers useful tools for the quantitative estimation of water content in a insulating solid materials. However, the correlation between electromagnetic characteristics and the amount of water in solids needs to be characterized using precise direct measurement methods. In this study, a two-port coaxial transmission cell has been characterized for water content estimation based on a study with the thermo-coulometric water detection method. The latter allows us to determine the proportions of the different water bonding forms that can exist in the material. The purpose of this paper is to provide a dielectric relaxation behavior study of the kaolinite clay from 10 MHz to 1.5 GHz, which was preceded by an experimental analysis of α-D-lactose monohydrate and the calcium oxalate monohydrate, which have stable water content under various humidity conditions.

1. Introduction

The water content is a key parameter in several domains such as industrial production processes, pharmaceuticals and civil engineering. Consequently, the number of studies and the amount of research in this field is constantly increasing in recent years, especially to measure the quantity of water which is difficult to access, usually named bound water. In the case of soil science and geology, bound water can be defined as the water held in soils by molecular or electromolecular forces [1]. On the other hand, free water is defined as the water that is related only by the gravitational forces in the clefts and macropores and can be evaporated without external energy.

In order to quantify the different types of water bonds in solids, usually Thermal analysis (TA) methods [2, 3] as well as the chemical methods like Karl Fischer titration [4] are used as references techniques.

For indirect methods, NMR relaxation measurements [2] and 1D magnetic resonance imaging [5] have been used to estimate free and bound water fractions in solides.

In terms of electromagnetic methods, the incomplete definition of the properties of bound water are discussed in [6]. However, the idea, that is widely accepted from a long time, that the relaxation frequency of bound water should be positioned between the relaxation of liquid water (10 GHz) and that of ice (5 kHz) [7].

In porous wet materials, the water movement is induced by different surface bonding forces due to interface processes [8–11]. Therefore, these interface effects cause an overlap of number of dielectric relaxations processes (free and bound water, Maxwell-Wagner and surface-polarization effects). All these relaxation processes are the effects of the particular deformations in the dielectric spectrum of the material at frequencies less than 1.5 GHz [1, 9, 12].

In addition to the aforementioned relaxation processes, the dielectric spectrum can be affected also by ionic conductivity. This is especially significant for samples with very high water content, where it masks all other phenomena. Hence, the contribution of this dc-conductivity can be easily identified by the change in the dielectric spectral behavior in low frequencies.

Therefore, in this work the two-port coaxial transmission cell (1"5/8) [13] has been characterized for water content estimation based on the complex relative dielectric constant measurement in the frequency range from 10 MHz up to 1.5 GHz.

In this study, kaolinite, with varying water content, α-D-lactose monohydrate and calcium oxalate monohydrate were investigated using the thermo-coulometric water detection method, which allows us to determine the proportions of various water bonding forms that can exist in the material (free and bound). The measurements made with this direct method were carried out in parallel and with the same samples that were measured with the coaxial cell.

2. Experimental methods

2.1. Sample preparation and experimental protocol

The samples studied were α-D-lactose monohydrate $C_{12}H_{22}O_{11}.H_2O$, CAS Number: 5989-81-1, calcium oxalate monohydrate $Ca\,H_2O_4.H_2O$, CAS Number: 5794-28-5, both from ACROS Organics and kaolinite clay $Al_2Si_2O_5(OH)_4$. The first material, is often used in the pharmaceutical field and in many dry food mixtures. Its key property is a stable low water content, around 4.9% (wet basis). This corresponds to the 'water of crystallization' and is strongly bound to the solid matrix. Therefore, this water cannot be released without heating the material [14–16].

$$C_{12}H_{22}O_{11} \times H_2O \longrightarrow C_{12}H_{22}O_{11} + H_2O\uparrow$$

The second monohydrate has a higher water content than α-D-lactose, around 13% [17]. As this material is only 98% pure, the impurities increase the probability of absorbing water from the environment. The latter would exhibit different properties from the monohydrate water as it's not bound by the same phenomena.

$$CaH_2O_4 \times H_2O \longrightarrow CaH_2O_4 + H_2O\uparrow$$

Numerous experiments using direct methods, both thermo-coulometric and loss-on-drying, with the monohydrate samples have established that the water content of these materials is distributed homogenously in the powdered material.

In this paper, all the reported measurements are carried out in an air-conditioned laboratory (temperature 20 ± 1 °C and air humidity 40 ± 4% RH). To have a better correlation between dielectric measurement and water content, the same sample is used in parallel in both coaxial cell and in thermo-coulometer.

2.2. Dielectric measurement using coaxial line

Measurements of the complex dielectric permittivity were made with the same two-port coaxial transmission cell (1"5/8 figure 2) in the frequency range between 10 MHz and 1.5 GHz using Anritsu MS2038C Vector Network Analyzer (VNA).

The sample for coaxial measurements is in the shape of hollow cylinder with an outer diameter of 38.8 mm and an inner diameter of 16.9 mm with a thickness equal to 3 cm (figure 1).

The calculation of the complex permittivity was made using the Nicolson- Ross and Weir (NRW) algorithm as described in [18–20] which correlates the S-parameters of the sample with the Transmission (T) and Reflexion (Γ)coefficient $|\Gamma| \leqslant 1$, and consequently with the complex permittivity and complex permeability, as described in the following equations:

$$\Gamma = \frac{1 + S_{11}^2 - S_{21}^2}{2S_{11}} \pm \sqrt{\left(\frac{1 + S_{11}^2 - S_{21}^2}{2S_{11}}\right)^2 - 1} \tag{1}$$

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} + S_{21})\Gamma} \tag{2}$$

$$\varepsilon_r^* = j\frac{c}{2\pi fL}\left(\frac{1-\Gamma}{1+\Gamma}\right) ln\left(\frac{1}{T}\right) \tag{3}$$

Where L is the sample length.

2.3. Thermo-Coulometric Water detection

To measure the water content and the proportions of the various water bonding forms that can exist in the materials, we used the thermo-coulometric technique. The instrument, $EasyH_2O$ one thermo-coulometer (Berghof Products +Instruments GmbH, Germany) uses a P_2O_5 sensor for the direct quantification of the water content via the Faradays law. An electric current occurs at the sensor is proportional to the mass of the absorbed water according to this equation:

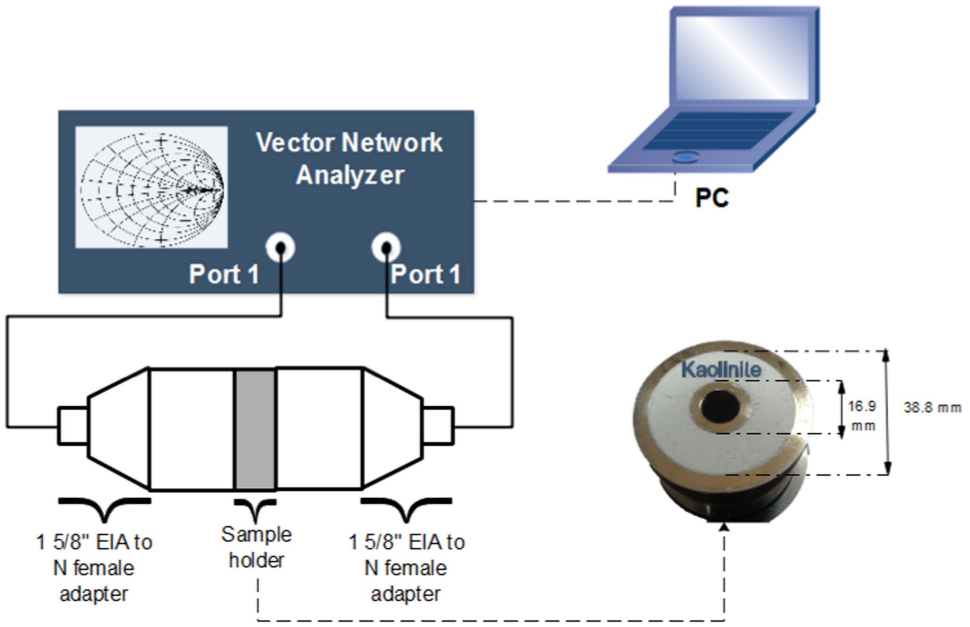

Figure 1. Schematic illustration of the dielectric measurement experimental setup.

Figure 2. Disassembled coaxial (1"5/8) cell.

$$I\Delta t = F\frac{m_{water}}{M_{water}}z \tag{4}$$

Where:

- I is the sensor electric current
- Δt is the time of analysis
- F is the Faraday constant
- m_{water} is mass of absorbed water
- M_{water} is the molar mass of water
- z is the number of electrons exchange

The specified sensitivity of the system is 1 μg of water, the applied carrier gas speed is 50 ml/min and the maximum heating temperature is 400 °C.

The instrument is controlled with Aqualys software. For reference measurements, a solid certified reference material with 1 g/100g water content was used (Water Standard Oven 1%, Merck KGaA, Germany). Samples were weighed on an AE240 analytical Mettler-Toledo International balance with 0.01 mg resolution.

By choosing appropriate temperature programs, the device allowed us to quantify separately different bounding forms of water, as illustrated by figure 3. To compensate for any water bound to the surface of the sample boat, a 'tare' measurement was also performed with an empty vessel. This result was automatically subtracted from the sample measurement.

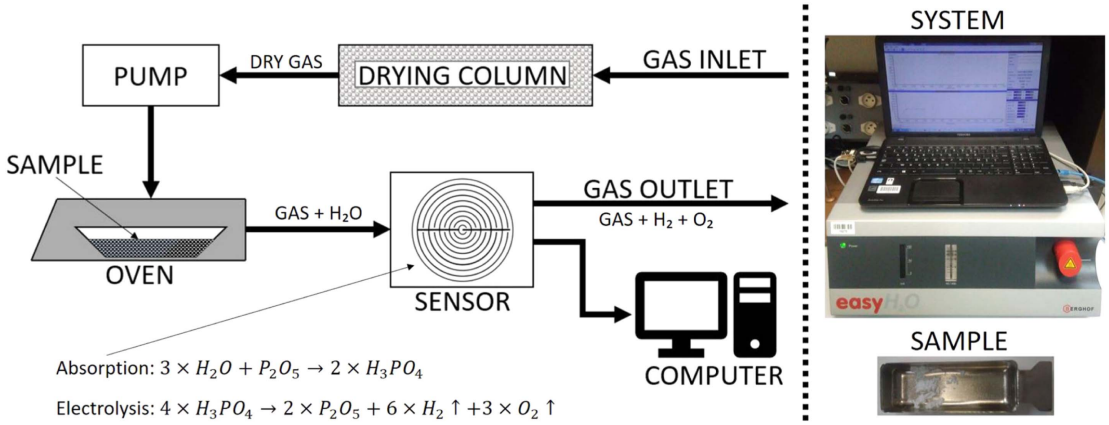

Figure 3. Schematic representation of the thermo-coulometric system.

3. Results

3.1. Model

As mentioned before (Introduction), it's known from literature that in wet porous materials (powder) multiple relaxation phenomena can intervene with the shape of the dielectric spectrum in addition to the dc-conductivity. To model these processes, several works use the sum of Debye, Cole-Cole, or Havriliak Negami (HN) relaxations. The last model is the most general in the case of a single relaxation. The experimental dielectric measurement results, both real part and imaginary part, are fitted using the sum of a maximum three HN relaxations. As it is known that the left slope of the non-relaxation peak can be described by the power law [21] that corresponds to the conductivity effect.

Results are fitted using Levenberg-Marquardt algorithm in Matlab using the following equation:

$$\varepsilon^* = \varepsilon'_\infty + \sum_{n=1}^{N} \frac{\Delta\varepsilon_n}{\left[1 + \left(j\frac{f}{f_{0n}}\right)^{a_n}\right]^{b_n}} - j\frac{\sigma}{\varepsilon_0(2\pi f)^m} \tag{5}$$

Where:

- f_{0n} : is the HN relaxation frequency (Hz) of the nth relaxation process
- ε'_∞ : is the high frequency limit of dielectric permittivity
- $\Delta\varepsilon_n$: is the dielectric strength of the nth relaxation process,
- σ: dc-conductivity
- $0 \leqslant a_n, b_n \leqslant 1$: HN stretching exponents

3.2. α-D-lactose monohydrate

3.2.1. Thermo-coulometric analysis

In this paragraph, we present the study and the identification of the bonding states in the α-D-lactose. The sensor current and the temperature profile for this analysis are presented in figure 4 below. From this result, we can conclude that this material doesn't contain free water, because below 50 °C there is no release of water from the sample. At higher temperatures the current starts to steadily increase and reaches its maximum value at 143 °C. This large peak corresponds to the loss of bound water confined in the crystal structure. As shown in figure 4, the water content of the α-D-lactose sample comes only from the bound water. The obtained average water content was 4.9 ± 0.22% at 95% confidence level. This is in good agreement with the values obtained by loss-on-drying (5.1%), reported by the manufacturer (4.9%, Karl Fischer analysis) and theoretical calculation (5.0%).

3.2.2. Dielectric permittivity results

Based on the study carried out previously with the thermo-coulometer, we can conclude the presence of a single type of water bounding form. The complex permittivity measurement results of the α-D-lactose monohydrate (figure 5) show a behavior change in low frequency range, especially around 7 MHz that can be correlated to the

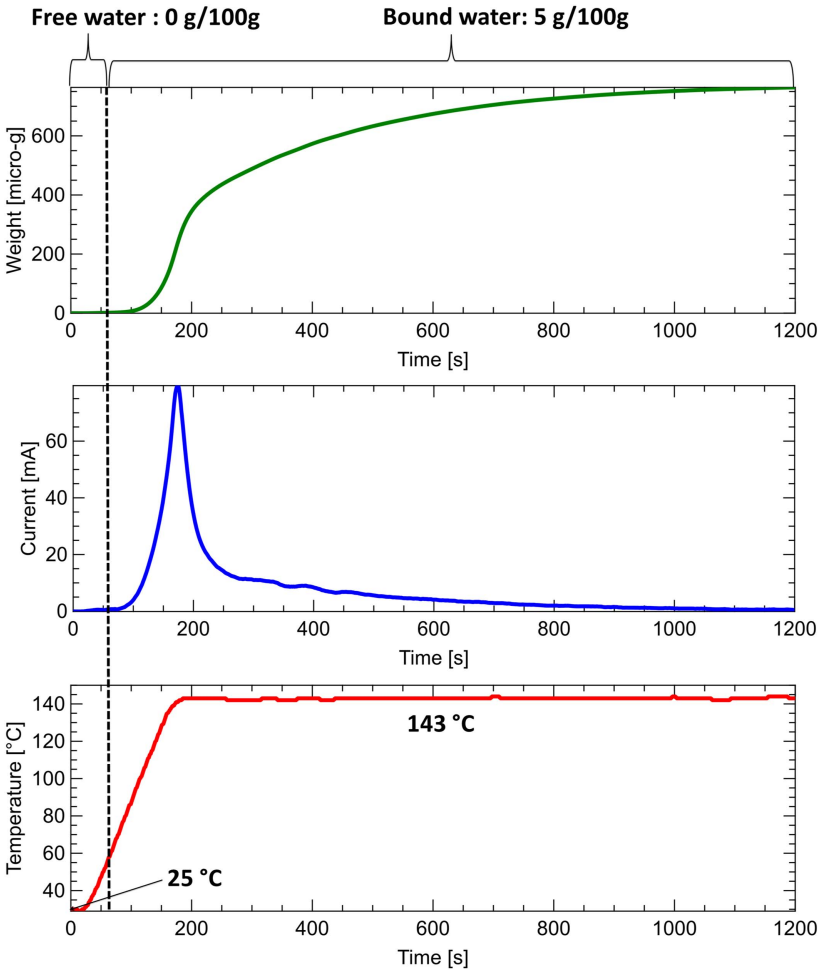

Figure 4. α-D-lactose monohydrate: the evolution of water from a sample as a function of temperature.

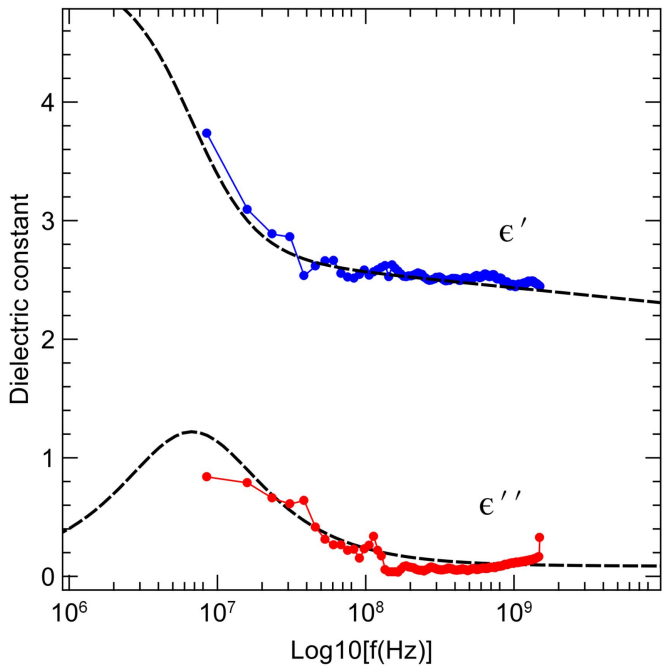

Figure 5. α-D-lactose monohydrate: The correlation between the complex dielectric measurement results and the model (dashed line).

Table 1. HN parameters.

f_{HN}(MHz)	$\Delta\varepsilon$	a	b	ε'_{∞}
6.72	2.286	0.134	0.431	1

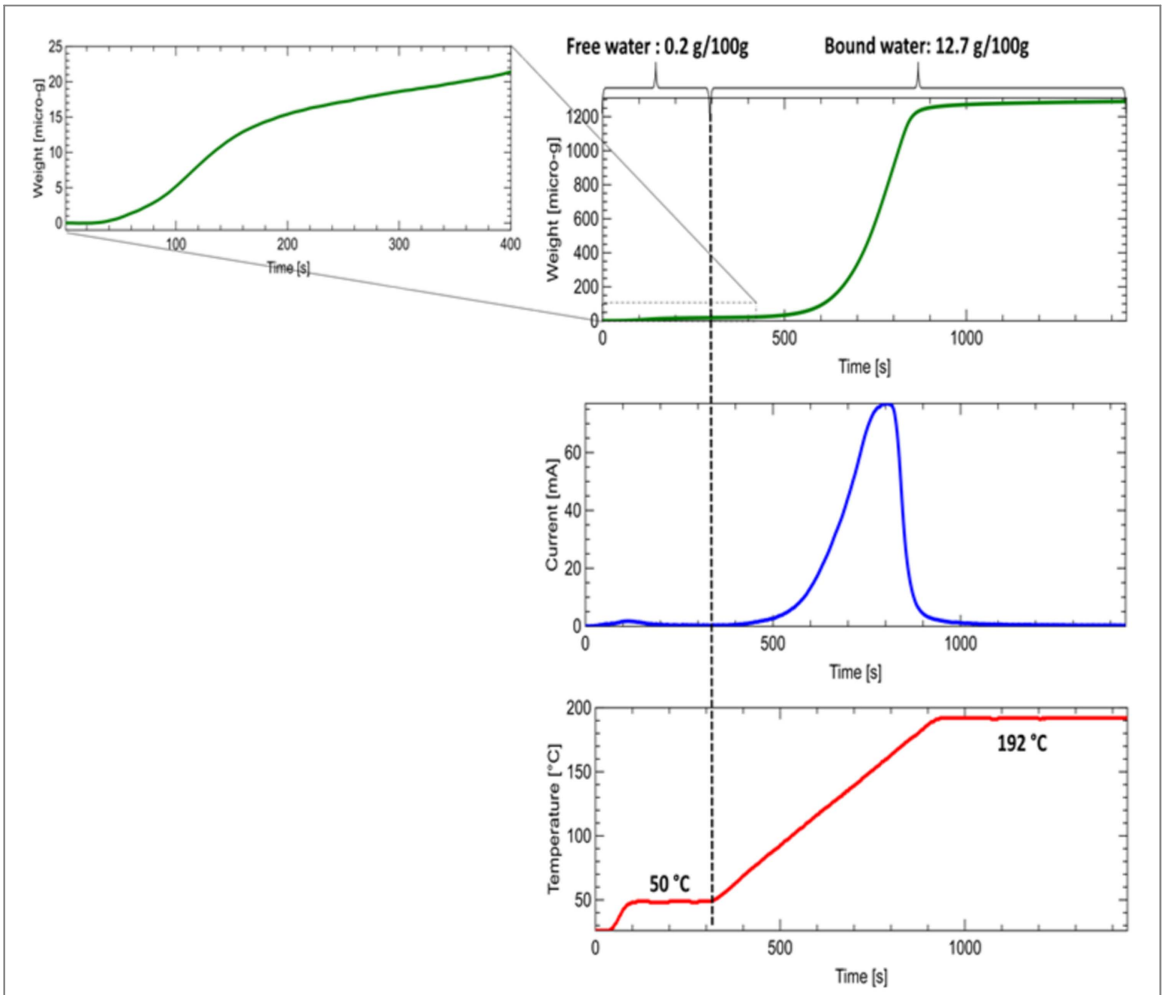

Figure 6. Calcium oxalate monohydrate: the evolution of water from a sample as a function of temperature.

bound water affect. On the other hand, comparing with the published measurement results in [22], we can find that the real part of the permittivity of α-D-lactose is between 2.6 and 2.7 in the same interval using an open-reflection resonator sensor. The measurement results can be modeled with a single HN relaxation process whose parameters are grouped in the table 1 below.

3.3. Calcium oxalate monohydrate

3.3.1. Thermo-coulometric analysis

In the case of calcium oxalate, we can conclude from the analysis results presented below (figure 6) that this material has a small amount of free water which can be measured separately. The majority of water can only be removed at temperatures above 100 °C, which corresponds to the water of crystallization.

The total measured water content of 13% is in good agreement with the value given by the manufacturer (13%). The theoretical value (12%) differs somewhat, but this doesn't account for any water coming from the impurities.

3.3.2. Dielectric permittivity results

The results from thermo-coulometry indicate the presence of two types of water in this sample and that one of them (bound water) is significantly more abundant than the other.

The dielectric measurement result in the band from 10 MHz to 1.5 GHz with the coaxial cell, of a sample initial weight equal to 25.7 g. and a thickness of 20 mm, are presented in figure 7. The modeling of experimental

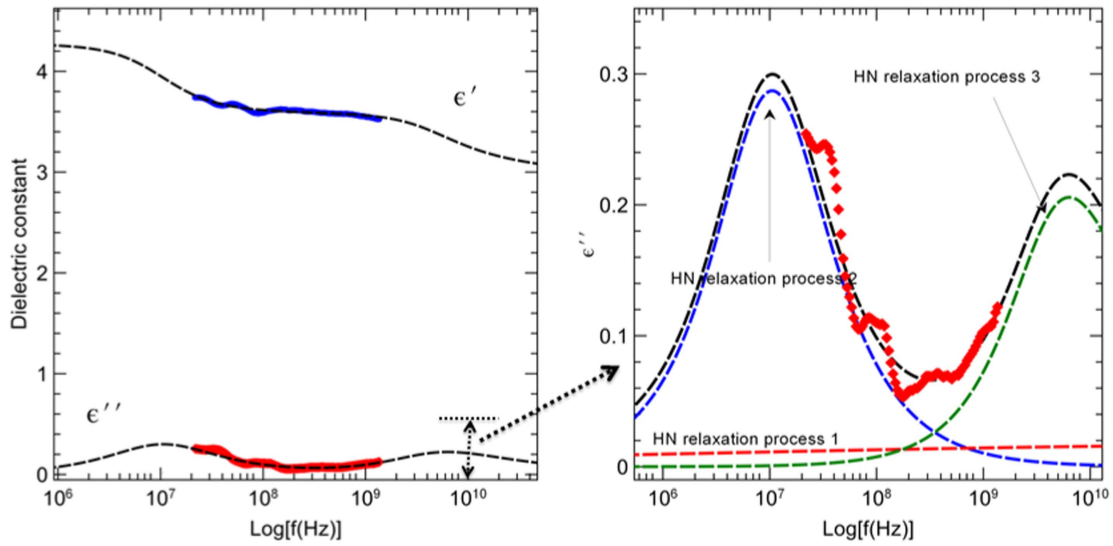

Figure 7. Calcium oxalate monohydrate: experimental complex dielectric permittivity measurement result with model (dashed line).

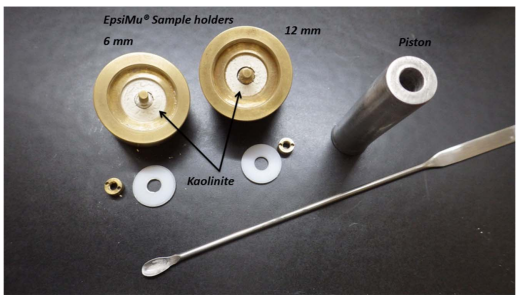

Figure 8. EpsiMu® sample holders and Teflon seals.

Table 2. HN parameters.

N	f_{HN}(MHz)	$\Delta\varepsilon$	a	b	ε'_{∞}	log10(σ_{dc})	m
1	10	0.640	0.948	0.94			
2	10.59	1.183	0.141	0.092	1.961	−34.58	2
3	4111.5	0.539	1	0.574			

results carried out with three relaxations whose fitting parameters are grouped in table 2; the most important are located at 10.59 MHz. This modeling may introduce an additional uncertainty component. However, it allows us to quantitatively relate this relaxation to the bound water, whereas the relaxation situated in the GHz zone is correlated to the free water.

3.4. Kaolinite

3.4.1. The effect of density

In this part, we focus the study on clay kaolinite. The first factor studied is the relative density of kaolinite. To investigate the effect of this factor on the dielectric permittivity, we use the EpsiMu® tool, which is formed of a coaxial cell with a diameter of 14 mm. The kaolinite used in these experiments is in the form of a fine powder. This material has a low moisture content (0.53%, wet basis). For performing EpsiMu® measurements, the sample holder is filled with the sample and compressed Applying different force for compressing allows to vary the density. The measurement cell has two Teflon sample closures that keep the sample in place if the density is very low (see figure 8).

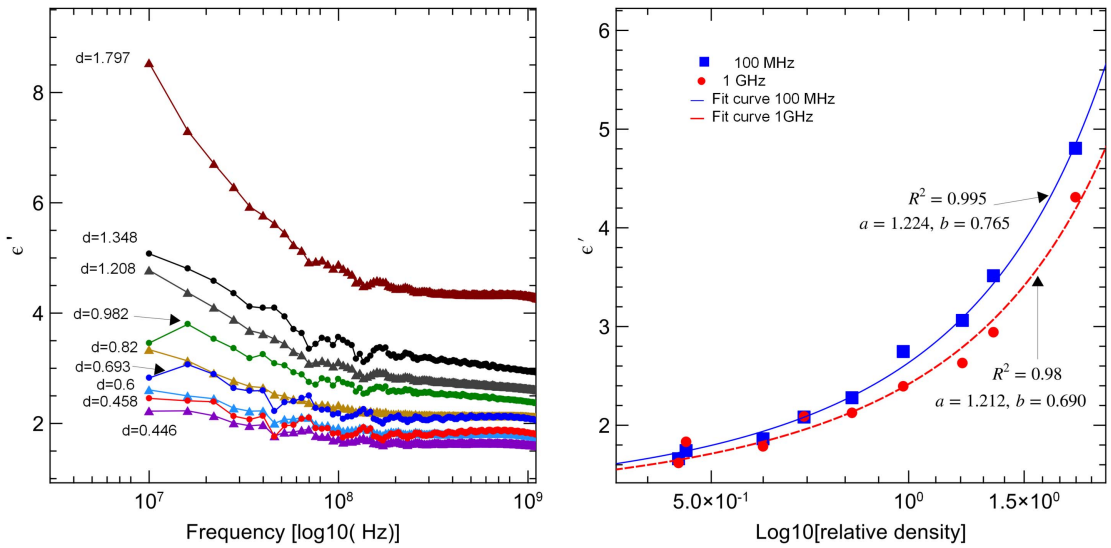

Figure 9. (left) The real part of permittivity measured in [10 MHz-1.5 GHz] with EpsiMu® with different relative densities, (right)Real part of the kaolinite measurement at 100 MHz and at 1 GHz as function of the relative density in logarithmic scale, results fitted using $\varepsilon' = ae^{bd}$ with d is the relative density.

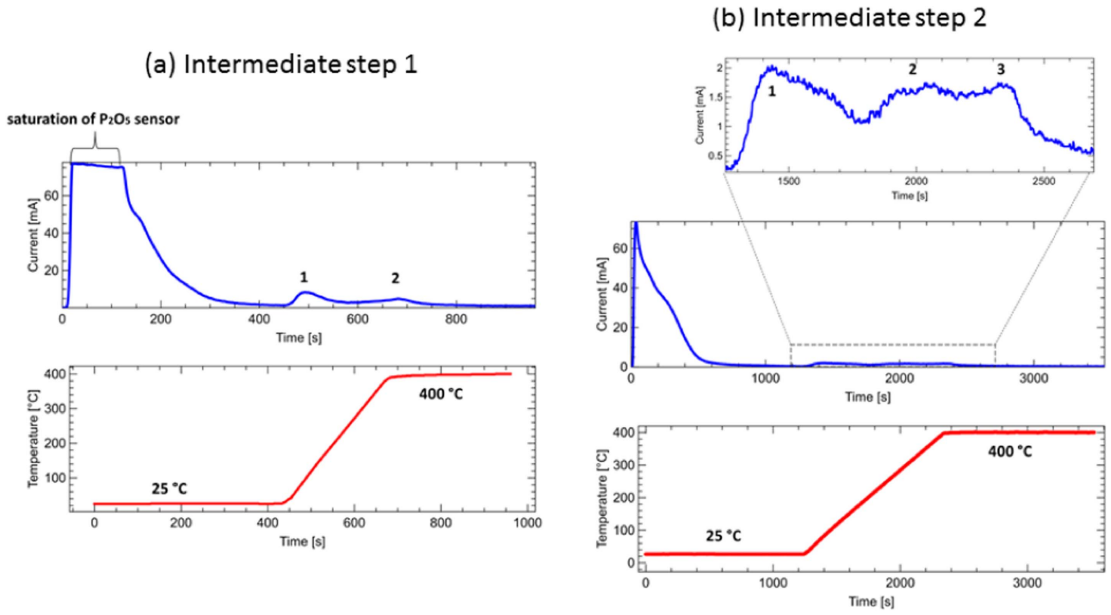

Figure 10. Kaolinite clay water quantification (a) Intermediate step 1, (b) Intermediate step 2.

The results of measurements with different densities (see figure 9) clearly show a relationship between these two parameters and allow us to model the permittivity of kaolinite according to an empirical model $y = ae^{bx}$ where y is the real part of permittivity and x is the relative density.

3.4.2. Thermo-coulometric analysis

In order to study how the water is released from the sample as a function of temperature, multiple experiments were carried out with various temperature programs. We were able to study its behavior in the temperature range between 25 °C and 400 °C, as this is the working range of the used instrument.

The thermo-coulometric water detection results presented in our work are tacked after many intermediates experimental steps using a temperature profile that systematically varied without heating steps to identify the number of the binding state that may exist in the material.

Two intermediates experimental results are presented in figure 10 that we realized to discriminate between the different bonding forms of the water in the kaolinite clay. In the first step (figure 10(a)), we change the

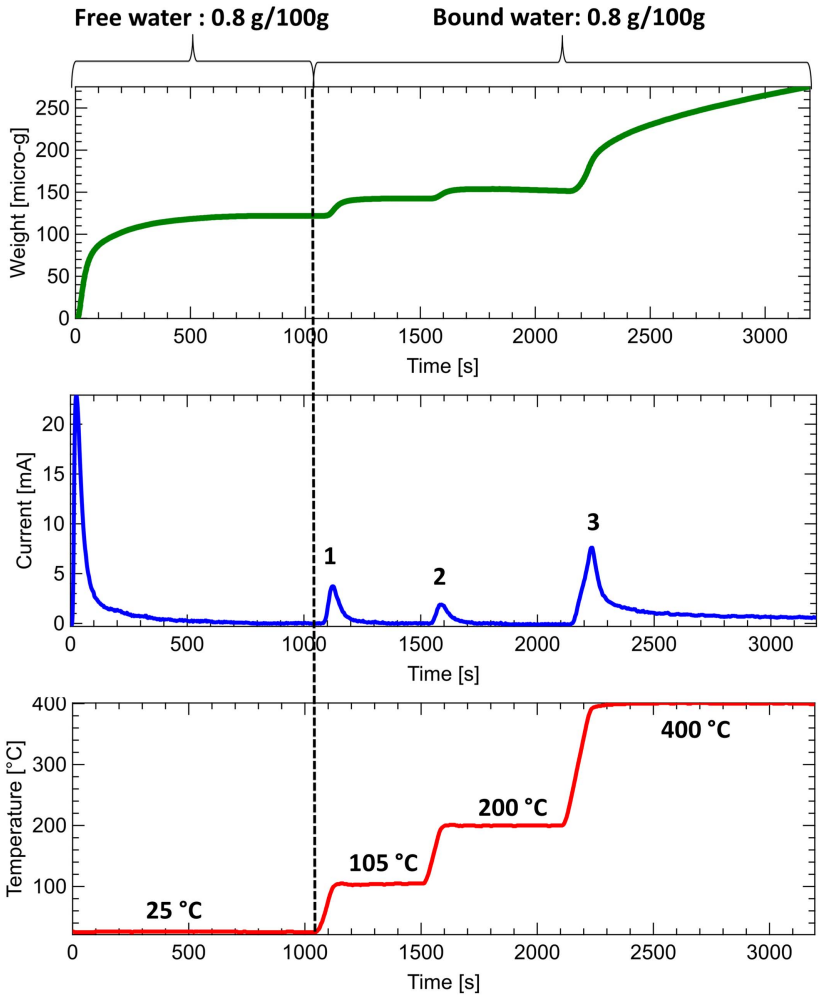

Figure 11. The evolution of water from a kaolinite sample as a function of temperature (1.6% total water content).

temperature with a faster speed (in 3 minutes from 25 °C to 400 °C), two types of bound water are detected witch are evaporated at 105 °C and 388 °C.In addition, the free water that it is released at 25 °C with an air flow (remark: the maximum value remains constant for 2 min because of the saturation of the P_2O_5 sensor with high water content). In another intermediate step (figure 10(b)), after removing the free water at 25 °C, we have changed the heating rate (in 20 min from 25 °C to 400 °C) and from this rate of drying in the thermo-coulometer, we start to visualize the presence of three peaks which corresponds to three different states of water bonds.

After the identification of the different types of water bonds with the dynamic temperature regime, we move to static temperature in order to determine quantitatively the fraction of each water bonding forms Within this temperature range we identified 4 different stages of water release from the kaolinite sample, as illustrated by figure 11. The first releases start at 25 °C, only by introducing the sample into a dry environment. It corresponds to the free water (or water of gravity) in the clay that can be removed with very weak forces. The other peaks correspond to differently bound forms of water (capillary water, hygroscopic water) as they can only be evaporated by increasing the temperature. The presence of four peaks is supported by calculations made by Smirnov and Bougeard [23] and a comprehensive study by Costanzo *et al* [24].

3.4.3. Dielectric permittivity results

To study the dielectric constant of kaolinite, we performed a series of measurements of six different samples. As we have previously studied the effect of the density of this clay, and considering that the process of filling the sample carriers requires compaction, in this paragraph we use the volumetric water content, $\theta(\mathrm{cm}^3\ \mathrm{cm}^{-3})$. The results of measurements of the dielectric permittivity are presented below, figure 12 presents the results for $\theta = 0.0474$ cm3/cm3 as well as the modeling result with HN model fitted to the measurement results.

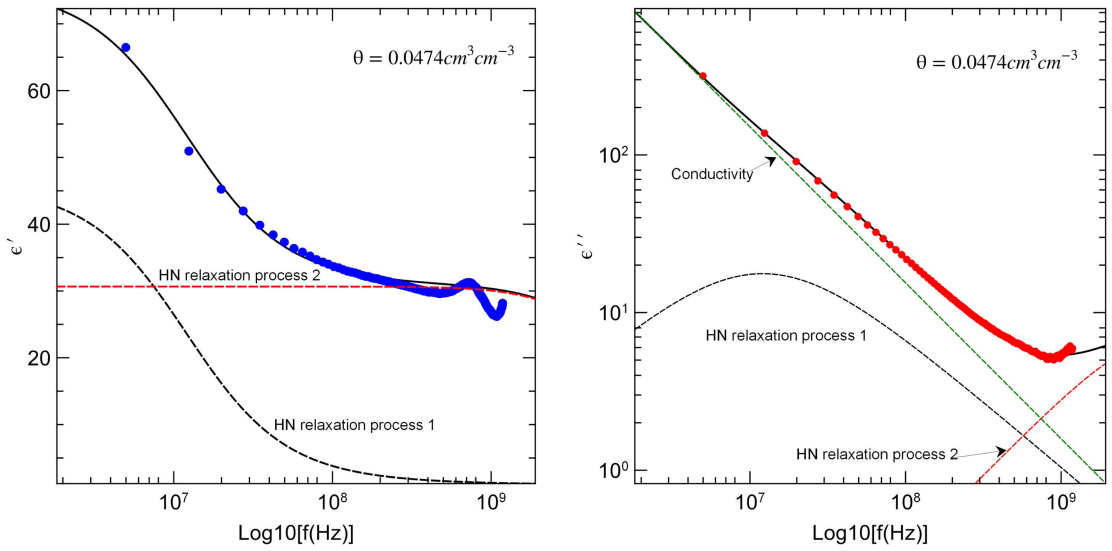

Figure 12. Dielectric permittivity measurements of kaolinite sample ($\theta = 0.0474$ cm3/cm3).

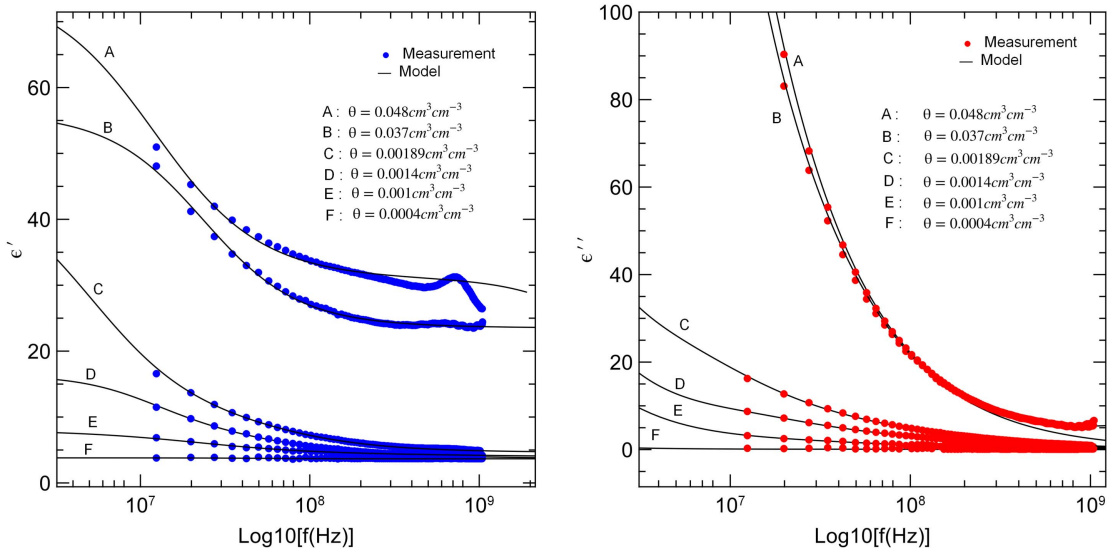

Figure 13. Experimental and modeled results for different wet kaolinite samples.

The modeling result shows the presence of two relaxations which are well separated. The first is situated towards the 50 MHz and another towards the GHz region. Based on the kaolinite clay study carried out by Ishida *et al* [10], which shows the same relaxation processes using the time-domain reflectometry method, we can associate the relaxation in the low frequency to the bound water and the other with free water.

Figure 13 shows the set of measurements made with kaolinite from the very moist sample measurements to the lowest possible proportion of water. The sample is weighed after each measurement. At the same time a small sample is taken for thermo-coulometric analysis.

In figure 14, we have presented the variation of the first dielectric strength of the relaxation process located in the MHz band which is easily identified as a function of the fraction of the bound water in the kaolinite clay measured with the thermo-coulometer.

The dielectric strength as a function of the fraction of bound water, shows a correlation in the part where the bound water is the most important (case of low water content)and a curve parallel to the abscissa axis which shows a non-correlation in the high water content (where the free water is the most important).

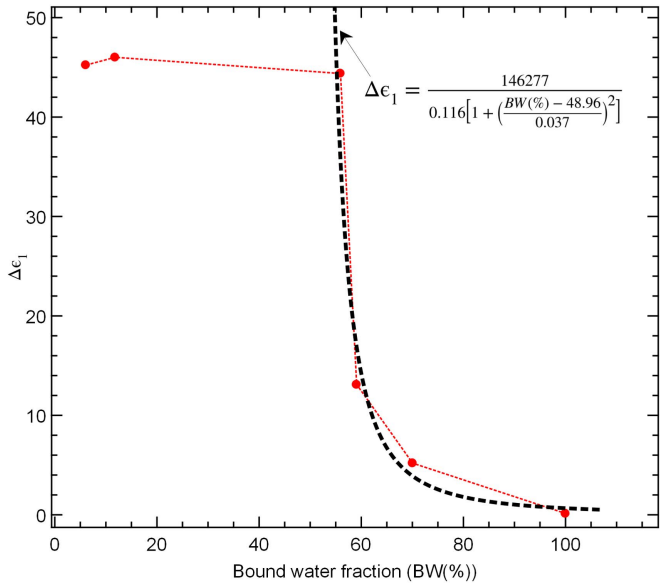

Figure 14. First dielectric strength (MHz) as a function of the fraction of the bound water in kaolinite clay.

4. Conclusion

Combining dielectric and thermo-coulometric methods, we have demonstrated the quantification of free and bound water in a number of materials through iterative development. The dielectric behavior of samples with one type of water (α-D-lactose monohydrate) or multiple types of water (kaolinite clay) were successfully modeled and related to both the types of water present and the overall water content. This work is a continuation of the study that we carried out on cardboard [11] with an attention on some powdered materials. These preliminary results serves as an avenue for further research into the relationship between free and bound water, rapid and selective water determination in additional materials of interest and the identification of different types of water in solids.

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