

# Quartz Crystal Oscillator Sensor for QCM Monitoring of Water Absorption in Anticorrosion Cataphoretic Paintings

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**Abstract**—With the objective of monitoring the water-uptake kinetics in anti-corrosion cataphoretic paintings, a quartz crystal microbalance (QCM) oscillator sensor was developed based on a 5MHz AT resonator. The sensor was experimentally characterized with the aim of determining its own sensitivity, phase noise and resolution during the water uptake process. Water uptake of the coating was investigated using the sensor, and results were compared with electrochemical impedance measurements.

## I. INTRODUCTION

Water absorption is an essential parameter to define the protection properties of anticorrosive paints. This parameter is often evaluated by means of the dielectric capacitance of the coating [1]. The presence of water in the coating increases its dielectric constant. The semi-empirical Brasher-Kingsbury equation allows the estimation of water uptake in coatings through capacitance measurements [2]. However, the capacitance of a coating depends, at least, on both the amount of water (volume fraction) and the shape of the water inclusions. Brasher-Kingsbury approximations may result in highly inaccurate values. Therefore, it is interesting to have a direct measurement of the mass increment of the coating together with the time evolution of its dielectric capacitance. With this objective, a Quartz Crystal Microbalance (QCM) electronic oscillator optimized to work in liquid medium was developed based on a 5MHz AT resonator [3]. The oscillator was used as QCM sensor to measure water uptake in a cataphoretic organic coating. The acoustic impedance and viscoelastic properties of the film were determined in order to assure the gravimetric regime during the water uptake process. The phase noise performance of the oscillator has been investigated in order to characterize the oscillator's resolution during the water uptake process [4]. Water absorption and desorption in the coating were investigated for two hours. Electrochemical impedance measurements were carried out during the water uptake. An equivalent circuit with two

hierarchically distributed parallel RC components was used to determine changes in the capacitance of the coating due to water uptake. Finally, the Brasher-Kingsbury equation was used to determine the evolution of the water uptake, and results were compared with the QCM ones.

## II. THE QUARTZ CRYSTAL OSCILLATOR SENSOR

A 5MHz QCM oscillator sensor based on Miller topology was designed to work in liquid [5]. The passive and active components were optimized so that the oscillation condition stays with the damping of the resonator caused by the fluid environment [3][6]. Copper electro deposition was used to perform an electrochemical calibration of the sensor with the purpose of determining the sensitivity coefficient (Fig. 1). An experimental coefficient of 57 Hz/( $\mu\text{g}/\text{cm}^2$ ) was obtained.

### A. Frequency noise and resolution

The resolution of the sensor for the organic coating-quartz crystal system in water was determined through the study of the phase noise of the designed oscillator [7][4]. The time domain characterization was done by directly measuring the oscillation frequency by means of a frequency counter

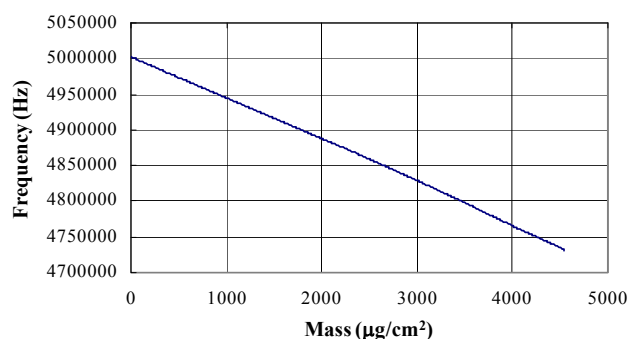


Figure 1. Calibration of the oscillator sensor with electro-deposited mass of Cu.

TABLE I. RESOLUTION OF THE SENSOR IN FUNCTION OF THE MEASUREMENT INTERVAL ( $\tau$ )

$\tau$	$\sigma_y(\tau)$	Detection Limit (Hz)	Resolution
2h 46m	$1.7 \times 10^{-7}$	0.840	15 ng/cm <sup>2</sup>
2h	$1.3 \times 10^{-7}$	0.650	11 ng/cm <sup>2</sup>
1h	$8.9 \times 10^{-8}$	0.445	8 ng/cm <sup>2</sup>
30m	$6.2 \times 10^{-8}$	0.310	5 ng/cm <sup>2</sup>
1m	$1.4 \times 10^{-8}$	0.070	1 ng/cm <sup>2</sup>
30s	$8.3 \times 10^{-9}$	0.042	728 pg/cm <sup>2</sup>
10s	$5.3 \times 10^{-9}$	0.027	465 pg/cm <sup>2</sup>
1s	$4.1 \times 10^{-9}$	0.021	360 pg/cm <sup>2</sup>

(Agilent 53131A). For a period of three days, the measurement was carried out under the conditions of application of the sensor: quality factor of the resonant system quartz-coating-distilled water,  $Q = 1372$ , water temperature stable at 31°C, and oscillator temperature stable at 41°C. 259200 samples of frequency were taken with a measurement interval of 1 s without dead time. Fig. 2 shows the frequency variation of the sensor between days 9 and 11 of immersion. At day 8, the coating was considered water saturated (see below the kinetics of water absorption in the experimental results section); therefore, the water uptake during the noise measurement can be neglected. The characterization of the long term noise was achieved via calculation of Allan deviations obtained by using an averaging time,  $\tau$ , from 15 to 9960 s. On the other hand, the first 1200 samples of frequency were used to determine the short term noise by computation of Allan deviations with an averaging time ranging from 1 to 46 s (Fig. 3). The maximum value of the deviation was taken to determine the resolution in the worst case. The uncertainty found is  $1.7 \times 10^{-7}$  for an averaging time of 9960 s (2h: 46min). Through this value, a detection limit of 0.84Hz, to which corresponds a resolution of 15ng/cm<sup>2</sup> (resolution for a 2h: 46min sampling time), was obtained. For an averaging time of 1 s, the deviation is, however,  $4.1 \times 10^{-9}$ . Therefore, the detection limit is 0.021Hz and the resolution of 360pg/cm<sup>2</sup> for measurements is carried out every second. Table I summarizes the resolution of the sensor for different measurement intervals.

#### B. Cathaphoretic painting deposition on the quartz electrode. Acoustic impedance and complex shear modulus

With the aim of obtaining a uniform thickness layer, 57 V were used for five minutes in order to deposit the cataphoretic coating on the quartz electrode. After the deposition, the coating was cured in oven at 180 °C for 15 min. WYKO-NT1100® optical profiler was used to measure the thickness of the coating. Results are shown in figures 4b and 4c. The averaged thickness was 11μm (50% of the nominal thickness used in automobile industry). Figure 4d shows a three-dimensional picture of the coating, where the homogeneity of the thickness in the active area can be noticed. The mass of the organic film was determined by the difference between the weight of the resonator before and after the coating application. As 3.1 mg was deposited on the 1.47 cm<sup>2</sup> surface,

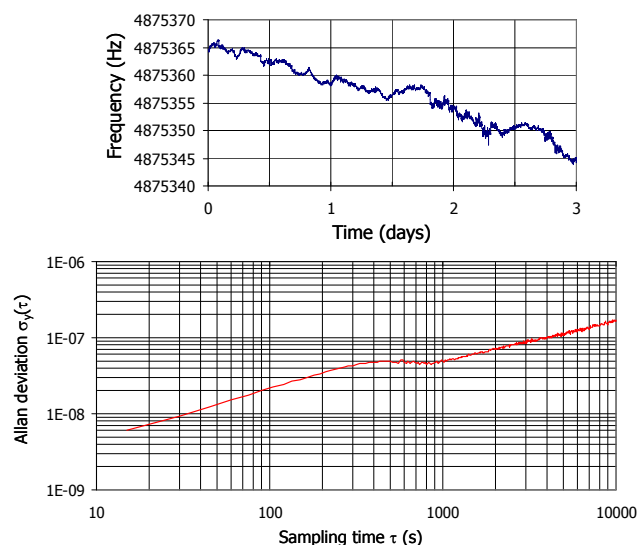


Figure 3. Frequency variation of the QCM oscillator with the organic coating between days 9 and 11 of immersion in distilled water, and long term phase noise.

the surface density is 2.1 mg/cm<sup>2</sup>. The result was corroborated by the resonance frequency value before and after the application of the coating. The volumetric density of the painting is therefore 1.91 g/cm<sup>3</sup> (for 11μm thickness). Since the thickness of the quartz crystal is 333 μm and its density is 2.651 g/cm<sup>3</sup>, 88.2 mg/cm<sup>2</sup> is the resulting normalized surface density. The relationship between the normalized surface density of both the organic coating and the quartz is therefore  $2.1/88.2=0.024$ , which allows the use of the Sauerbrey relationship to determine the mass added to the resonator from the crystal's frequency variation with insignificant error (small mass approximation) [8, 9]. Although the deposited film cannot be considered as a rigid mass, the energy loss of the shear wave of the QCM resonator into the organic film is

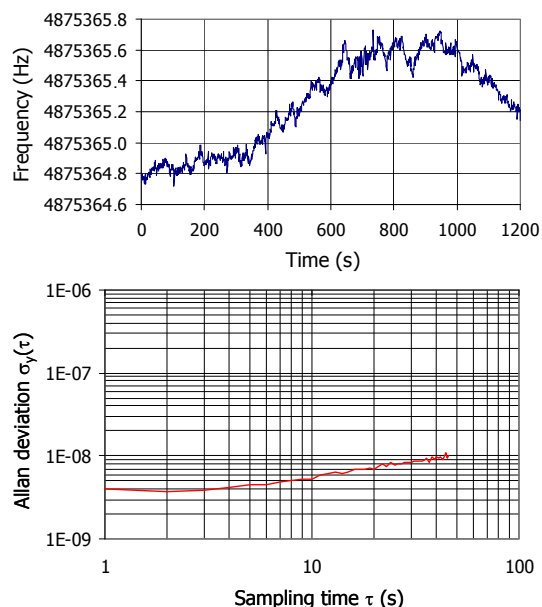


Figure 2. Short term frequency variation and corresponding phase noise.

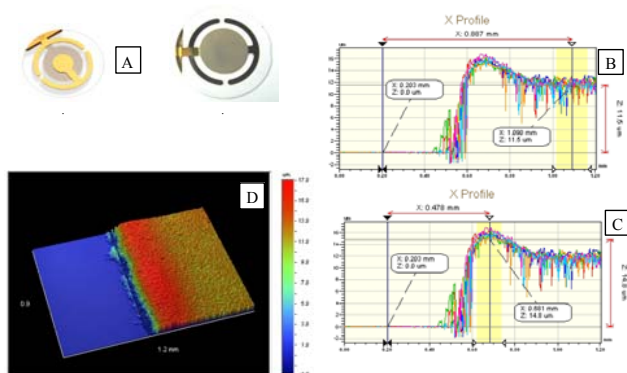


Figure 4. Cathaphoretic painting deposition. a) Aspect of the painted electrode. b) Interferometric profile showing the averaged thickness. c) Interferometric profile showing the thickness of the border. d) Three-dimensional image of the organic coating obtained by interferometry

insignificant for small mass loads. Therefore, it does not affect the frequency measurement, so that the resonator behavior follows the Sauerbrey relationship. The (complex) acoustic load impedance and the (complex) shear modulus of the paint were also calculated before and after de water uptake in order to determine if transition from glassy to rubbery behavior occurred during the water sorption [10]. Table II shows the obtained values calculated from the resonance frequency of the coated quartz crystal. These values confirm that the coating has glassy consistence and that the water uptake does not lead to significant changes of modulus. Besides, the phase shift of the acoustic wave while travelling through the coating ( $\phi$ ) and the acoustic factor ( $V$ ) were also calculated. These values are summarized in table II. The real part of the acoustic factor approaches to one and the imaginary part approaches to zero, which confirms the gravimetric regime of the sensor [10].

### III. QCM MONITORING OF WATER ABSORPTION

The painted quartz was immersed in water at 31°C for 2h. Frequency samples were carried out every second, which gives a resolution of 360pg/cm<sup>2</sup>. Figure 5 shows the frequency changes and their interpretation as mass (water) changes in the cataphoretic coating according to the Sauerbrey relationship with a sensitivity of 57 Hz/(μg/cm<sup>2</sup>). Their behavior corresponds to the prospective one for this type of

TABLE II. ACOUSTIC IMPEDANCE AND VISCOELASTIC PROPERTIES OF THE CATHAPHORETIC PAINTING BEFORE AND AFTER UPTAKE (IMMERSION OF 2H IN DISTILLED WATER)

	Acoustic impedance	Complex Shear Modulus		Phase shift	Acoustic factor	
	$Z_L$ (kg m <sup>-2</sup> s <sup>-1</sup> )	$G' + j G''$	$G' \quad G''$	$\phi$	$V$	
		(Pa)	(Pa)			
Before water uptake	5.35E3 + j 5.37E5	1.98E9	8.45E8	0.264 - j 0.054	1.023 - j 0.010	
After water uptake	6.09E3 + j 5.39E5	1.71E9	7.10E8	0.285 - j 0.057	1.027 - j 0.012	

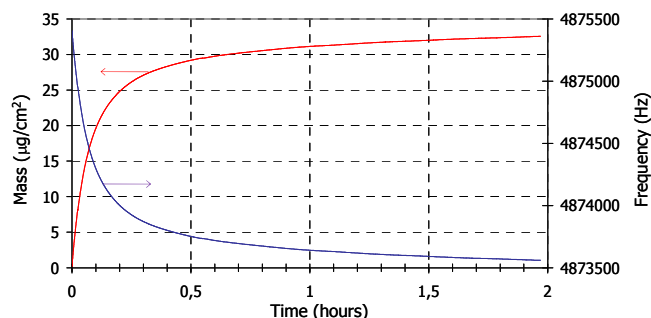


Figure 6. Kinetics of water uptake in the coating followed by the QCM oscillator sensor

systems [9][1]: a rapid increment of the mass (water) followed by a period where the rate of mass gain decreases until an input/output dynamic equilibrium is reached.

On the other hand, electrochemical impedance measurements were carried out during the water uptake under the same experimental conditions and compared with the QCM measurements. Figure 6 shows both real and imaginary components of the impedance of the interface resonator-organic coating-water for the first two hours of immersion in distilled water. The low frequency impedance limit decreases quite fast for the first hour and more slowly later, in a way comparable to the frequency increasing observed in Figure 5.

The equivalent circuit displayed in figure 7 was employed to model the behaviour of the paint. This consists in two RC elements hierarchically distributed.  $R_e$  accounts for the electrolyte resistance. The high frequency time constant,  $R_p C_p$ , is related to the dielectric properties of the paint and hence with the barrier properties. It is well-established [1][11] that the changes in the capacitance of the coating ( $C_p$ ) and in the pore resistance ( $R_p$ ) are due to water uptake process. The low frequency time constant  $C_{dl} R_{ct}$  is associated with the interfacial processes developing at the gold – paint interface. The  $\alpha_i$  parameters account for the Cole-Cole dispersion of the  $R_i C_i$  time constants. Eqs. (1) and (2) correspond to the impedance of the equivalent circuit depicted in figure 7. The

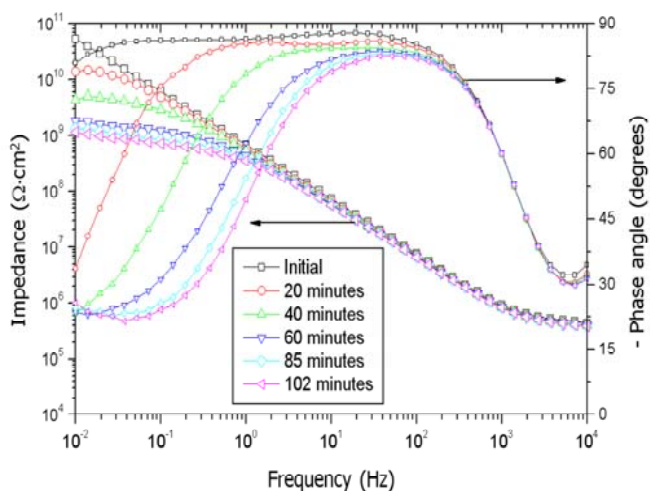


Figure 5. Evolution of the impedance of the resonator with the organic coating for the first two hours of immersion in distilled water

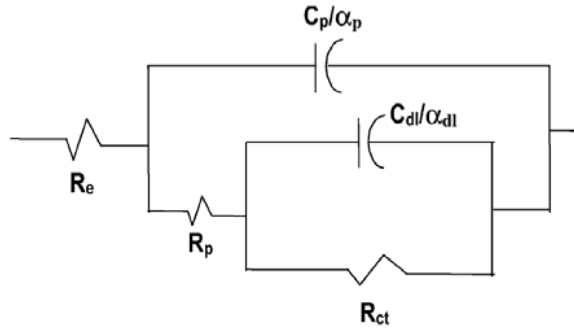


Figure 7. Equivalent circuit employed to model the paint behaviour.

capacitance values obtained by a nonlinear least squares fitting procedure [11] are depicted in Figure 8.

$$Z(\omega) = R_e + \frac{R_p}{(j\omega R_p C_p)^{\alpha_p} + \frac{1}{1 + Z_2/R_p}} \quad (1)$$

$$Z_2(\omega) = \frac{R_{ct}}{(j\omega R_{ct} C_{dl})^{\alpha_{dl}} + 1} \quad (2)$$

It is possible to correlate those capacitance values with the volume fraction of water using the Brasher-Kingsbury empirical equation:

$$X_v(\%v/v) = \log(C_t/C_o)/\log \epsilon_{H_2O} \times 100 \quad (3)$$

where  $C_t$  and  $C_o$  represent the capacitance at an instant  $t$  and for the “dry” coating, respectively,  $\epsilon_{H_2O}$  the dielectric constant of water (77 at 31°C), and  $X_v(\%v/v)$  is the water content (volume fraction in the coating). Figure 8 shows the evolution of the water uptake obtained by this procedure for the first two hours of immersion. One can observe that, as in

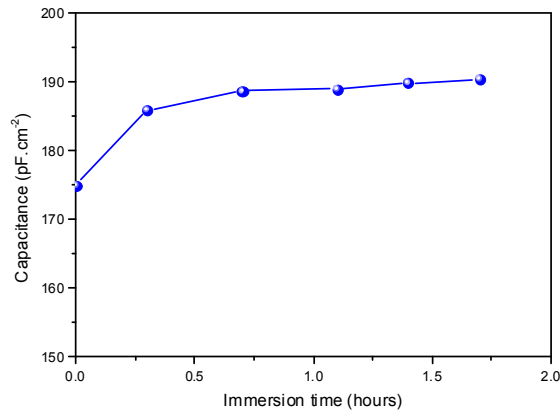


Fig. 8. Coating capacitance evolution for the first immersion hours.

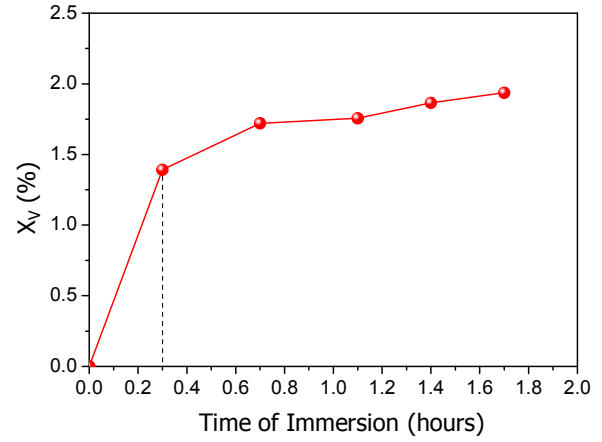


Figure 8. Evolution of the water uptake into the organic coating for the first two hours of immersion (derived from the Brasher-Kingsbury equation).

Figure 5, the 30 initial minutes correspond to the period where it reaches about the 90% of the total amount of water that comes into the film.

Although the trend obtained for water sorption into the polymeric film is similar in both methods (figure 5 and figure 9), an interesting discrepancy exists between the absolute values obtained. From Figure 5, at 1.4h immersion the water into the coating is 32  $\mu\text{g}/\text{cm}^2$  which, taking into account the working area and the thickness of the polymer, 1.47  $\text{cm}^2$  and 11  $\mu\text{m}$ , respectively, results 0.0290 g of water absorbed by cubic centimeter of the polymer. Assuming 1  $\text{g}/\text{cm}^3$  as the value of water density, we get 2.9% water ingress.

From figure 9 water ingress at 1.4 h is 1.85%, thus a factor 1.15 between both values. In order to match the data in figure 9 with those given in figure 5 it is necessary to assume that the dielectric constant of water,  $\epsilon_{H_2O}$  in eq. 1 is lower than 80 (16 in the present case). This proves that an important part of the water into the polymeric structure is present not as free water occupying empty voids or pores but adsorbed in the polymeric mesh so that the rotation movement is hindered, with the corresponding decreased  $\epsilon$  value ( $\epsilon_{H_2O}$  is about 3 for ice).

#### IV. CONCLUSIONS

A stable oscillator for liquid environment was designed to follow the water uptake in films of organic coatings. The oscillator can detect variations of water uptake (mass) up to 360pg/cm<sup>2</sup> in one second. With this study, the power of the oscillator sensor as a tool for monitoring of water absorption in anti-corrosion organic coatings is illustrated. In addition, this sensor provides quick and reliable information regarding water absorption which is one of the more important factors in the definition of the protection properties of anticorrosive paints.

#### ACKNOWLEDGMENT

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