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Impedance analysis of varnish-modified crystal quartz resonators coupled with FT-IR and FT-Raman: Assessment of the environmental impact on artistic materials in conservation sites

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Abstract

There is an increasing interest in analytical sensing systems for assessing the impact of the environment on the materials of the cultural heritage stored in indoor conservation areas. In this paper, the response of sensors obtained by coating quartz resonators with thin films of artistic varnishes (mastic and dammar), artificially aged under visible or UV radiation, is discussed in terms of their impedance curves around the resonating frequency. Electrodeless quartz crystals are used on account of their enhanced recycling simplicity and lower cost. The ageing under visible radiation induces a systematic negative shift (of the order of hundreds of Hz) and a damping of the impedance curve, with an increase in the impedance minima, which seems to indicate both gravimetric and visco-elastic effects. Controls exhibit only a minor shift, but again in the negative direction. On the other hand, under UV artificial ageing the frequency change is towards more positive values and is more substantial than in the case of visible light ageing. In these impedance spectra, although the overall frequency change appears to be more directly associated with the degree of ageing and/or degradation (thus being a potentially suitable parameter for continuous monitoring in field applications), the alterations in the shape of the curves are important to distinguish different types of ageing. The impedance analysis data is combined with the information retrieved from FT-Raman and FT-IR, also non-destructive techniques. A different rate of ageing, inferred by impedance analysis, is observed in the changes of specific band markers identified in the FT-Raman and FT-IR spectra. In particular, the higher reactivity of mastic versus dammar was highlighted by both methods.

Keywords: Cultural heritage; Impedance analysis; Environmental impact; FT-IR; FT-Raman

1. Introduction

Analytical chemistry plays an important role in the conservation of works of art inasmuch as it provides information on the composition of materials and their state of preservation, as well as on the extent and mechanisms of degradation. A full and reliable diagnosis on the “health conditions” of artistic artifacts is mandatory for effective preventive conservation and the definition of appropriate restoration strategies.

One important task is to explore the effect of environmental factors such as light, temperature, humidity and atmospheric pollutants on degradation processes [1–3]. Although the decay of materials in time is an inevitable process, a better understanding of their interaction with the environment is important to prevent accelerated deterioration and implement the conditions for maximising their effective lifetime. Besides, the conservator should ideally be able to assess the impact of the specific microclimates in which collections are stored and to recognise in time potential environmental risks [4].

The identification of early signs of materials degeneration is a goal that can be pursued by detecting changes in the materials at a molecular level. Recently, Odlyha et al. have proposed [5], tested and evaluated [6–9] the use of mock paintings as dosimeters of the overall effect of the environment on the degradation of artistic materials. These systems, consisting of variously pigmented tempera test panels, were first calibrated by artificial ageing and, then, exposed in real conservation sites. The chemical changes occurring in each paint stripe was quantified by scraping small

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portions of tempera and individually analysing them by direct temperature resolved mass spectrometry (DTMS), reflectance spectroscopy in the visible, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and FT-IR. The results, partly elaborated by statistical analysis, confirmed that the principle of dosimetry works since changes in the chemical composition of the paints were systematically correlated with the degree of ageing. Furthermore, the results pointed at the importance of the contribution of light in the degradation process, although there were evidences of the synergistic effect of other factors, mainly based on the observation that samples exposed in real conservation sites aged at a larger extent.

In another pilot study, sensors for continuous real-time monitoring of specific microenvironments of storage and exhibition sites [10] were devised by modifying quartz crystal microbalances (QCM) with a thin film of mastic varnish (widely used in paintings). The sensors were prepared by spray-coating one of the QCM surfaces with thin layer of the varnish. Subsequently, the natural and artificial ageing (under visible light) of the films was followed as shifts in the crystals oscillation frequency, which were consistently negative. The alterations in the oscillation of the varnish-modified resonators were quite clearly correlated with the film ageing. In this sense, the technique seemed to represent a convenient approach to measure the rate of the ageing process, thus providing a means for monitoring the potential impact of a specific environment. Yet, the technique did not provide any direct information on the actual structural changes taking place in the material, nor could it be obtained without sacrificing the sensor unless a non-destructive analytical method is adopted.

In the present work, Raman and FT-IR have been employed for this purpose. These analytical techniques were chosen because they allow extracting complementary structural information of the material's components without the necessity of sampling, i.e. preserving the integrity of the specimen, provided appropriate laser intensity is used [11,12]. In particular, for FT-IR analysis, the transmission mode was adopted and, for this reason, a film of varnish was directly deposited directly on KRS-5 disks, as described in Section 2.

Raman spectroscopy, on the other hand, presents a somewhat more distinct character of non-destructive technique as a genuine solid-surface technique based on the probing of emitted (scattered) radiation resulting from a laser-excitation process. This, as well as other additional features, already summarized by Edwards [11], have contributed to the increasing favour with which the specialists of the field of art preservation regard nowadays this technique as a valuable diagnosis tool [13].

The investigations described and discussed in this paper focussed on two natural resins (dammar and mastic) and were carried out by Impedance Analysis of electrodeless QCMs modified with thin films of the respective varnishes, as well as by FT-Raman and FT-IR. As shown in a few recent studies [14–16], the analysis of the impedance of (modified) QCMs – also sometimes referred to as QCM impedance spectroscopy – represents a convenient tool for investigating the alterations of thin films deposited on the crystal. The basis and potentialities of this technique have been thoroughly reviewed elsewhere [17–21] and therefore are only briefly summarised in the following lines.

When inserted in a suitable oscillating circuit, a properly electroded AT-cut quartz crystal becomes the frequency-determining element. In this electromechanical system, the electrical and mechanical frequencies coincide with the resonant frequency of the crystal. When the quartz resonator is operated in the contact with air, this property depends on constant properties of the quartz crystal (thickness, density and shear modulus) and on environmental factors normally held constant (pressure and temperature) and, therefore, its value is substantially very stable. In general, systems of this type are employed as very sensitive microbalances (hence the conventional denomination of QCMs) by inserting the quartz crystal in an oscillating circuit and monitoring changes in the oscillating frequency. Typical applications include the use as sensor of gaseous species upon adsorption of the analyte on selective polymeric sorbents immobilised on one of the crystal faces [20–22]. This sort of applications, which rely on the linear dependency between frequency and mass, mathematically traduced by the well-known Sauerbrey equation, are possible when the deposited layer is rigid and much thinner than the crystal (typically <2%). In the presence of visco-elastic films, that linear relationship is no longer valid, because those shifts can at the same time result from mass changes and alterations in the visco-elastic properties of the film.

Nonetheless, such changes in the physical properties of thin films associated with variations in their visco-elasticity can be revealed by examining of impedance versus frequency spectra recorded around the resonance frequency by an impedance analyser. A rigorous treatment (network analysis) implies that the (modified) QCMs be traduced in terms of their equivalent electrical circuits (Butterworth–Van Dyke models, e.g. see [18]). In particular, the resistive and inductive components are, respectively, associated with the visco-elasticity and the mass of the resonating system and can be used to quantify changes of that nature in the coating [16]. In a qualitative approach, however, the visco-elastic and the gravimetric changes in the film can be evaluated through the profile of the spectra and their positions along the frequency axis. As general rule, the former affect the shape of the curve and lead to its dampening, whereas the latter cause the shifting of the sigmoid signal towards lower or higher frequency values as the mass increases or diminishes [18].

As for the choice of electrodeless QCMs, adopted in this work, various authors demonstrated that the quartz crystals work as resonators even when the electrodes are simply placed at a short distance from the crystals, provided the gap is small enough [23,24]. This configuration adds a further capacitive contribution to the above-mentioned equivalent circuit. In practice, measurements can be taken using a suitable cell designed in such a way as to house the quartz disk closely sandwiched between the electrodes, such as that described by de Jesus et al. [24]. The main advantage is that the same crystal can be recovered and reused several times by removing the old coating, an operation that might damage the metal layer in electroded resonators. On the other hand, it must be borne in mind that the positioning in the cell is hardly reproducible and leads to a higher degree of between-measurements variability. In addition to that, in a strict