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Analysis of a royal 15th century illuminated parchment using a portable XRF–XRD system and micro-invasive techniques

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ABSTRACT

A system of complementary X-ray diffraction (XRD) and fluorescence (XRF) was used for non-invasive *in situ* identification of inorganic materials in a highly valuable illuminated parchment, now preserved at the Archive of the Royal Chancellery in Granada (Spain), via which King Enrique IV (1425–1474) conferred nobility on Gil Fernandez and Alonso Covo. The study of organic matter, by capillary electrophoresis (CE), could not be performed without taking microsamples that had also been used to confirm – by micro-Raman spectroscopy and scanning electron microscopy (SEM–EDX) – the nature of inorganic materials that had been identified by XRD–XRF.

Gold and silver were detected as well as lead tin oxide in yellow, azurite in blue, vermilion and minium in reddish colours and malachite in green. Calcite was applied to the entire sheets and gypsum to the text area. Iron-based ink was used for the parchment text. These analyses enable the document to be put into its historical context; they serve as a starting point in a comparative study with other similar documents, for the reconstruction of its documentary archaeology.

1. Introduction

Parchments were for many centuries the vehicle of culture and information throughout Europe at least until the end of the Middle Ages, when parchment was progressively substituted by paper (Pangallo et al., 2010). Parchments are made from the skin of sheep, goat or calf, and are commonly employed for codex or manuscripts, as a support for written documents and also for illustration purposes and as cover material in book-binding (Dolgin et al., 2009; Walczak et al., 2008). Illuminations are coloured adornments such as initial capital letters, fringes of text or miniature illustrations embellished with gold and/or silver. The illumination process was reserved for the most precious documents. The earliest surviving illuminated artworks date from the 5th Century, though it was not until about 12th Century that their production began to flourish in earnest. This 'golden age' of illumination lasted until the arrival of Gutenberg's printing press after 1450 (De Hamel, 2001).

Royal solemn privileges are the most important and solemn documents that were dispensed by the Royal Chancelleries in the Middle Ages with the purpose of manifesting the commitments of the Kings. In the Iberian Peninsula, these documents (known as *privilegios rodados*) were dispensed between the 12th and 16th Centuries. Their importance lies not only in their beauty, but also in that they provide a safe documentary basis for the reconstruction of the historical past. Their design, materials and content organization were subjected to a strict process. Pigments and dyes are the main components for producing the inks and paints. Due to their generally organic origin, most dyes are photosensitive and undergo tone/hue alteration over time. They are also altered by climate changes, and are very sensitive to restoration treatments and conservation conditions (Matteini and Moles, 2001). Binders of pigments and dyes are generally water-soluble; therefore, even the simplest water-based cleaning methods might dissolve them. All these phenomena make the identification of pigments and dyes a pre-requisite for any intervention on a document.

Illuminated parchments are difficult to analyse; they are unique works of art, made of extremely delicate materials, and, generally, institutions only permit their study *in situ* in order to prevent any damage caused by changes in temperature and humidity. In

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addition, the value of these objects makes their transportation risky and expensive, hence the development of portable analytical instrumentation that can be brought to conservation sites (museums, archives, libraries, etc.). Portable X-ray fluorescence (XRF) systems have been widely employed to ascertain the elemental composition of materials on illuminated parchments and manuscripts (Aceto et al., 2012; Bruni et al., 2008; Manso et al., 2013; Miliani et al., 2012; Van der Snickt et al., 2008). However, XRF is often not specific enough to identify these materials with certainty. The materials in heritage objects are most often complex mixtures including inorganic as well as organic materials. It is therefore necessary to use various experimental techniques. Recently, spectroscopic techniques have been extensively applied for the study of this type of artwork (Aceto et al., 2012; Manso et al., 2013; Miliani et al., 2012; Nastova et al., 2012; Pessanha et al., 2012). For inorganic matter, X-ray diffraction (XRD) is highly suitable for complementing XRF, by performing XRD and XRF at the same point where X-rays hit the artwork surface. Only a few portable XRD systems are available for phase identification, and limitations in terms of angular resolution and measurement times are often observed (Chiari, 2008; Gatto Rotondo et al., 2010; Gianoncelli et al., 2008; Sarrazin et al., 2008; Uda et al., 2005). A portable XRD/XRF equipment has been designed and built at the laboratory of the Centre de Recherche et de Restauration des Musées de France (C2RMF). This non-invasive analytical system has been tested on a large number of ancient artworks, mostly paintings and ceramics in various museums (Duran et al., 2010, 2011a; Eveno et al., 2010; Gianoncelli et al., 2008), but it has not been used on ancient illuminated parchments.

Organic dye identification cannot be performed by XRF–XRD; therefore, other analytical techniques have to be used. Capillary electrophoresis (CE) was selected because the method of analysis of dyes must be highly selective and sensitive due to the complexity of the matrices and the limited quantity of sample available. Particularly in the case of graphic documents CE has proven to be a very powerful tool; it allows the combination of short analysis times and high separation efficiency although a micro-sample is required (López-Montes et al., 2007). Taking advantage of the few micro-samples collected, Raman spectroscopy and SEM–EDX (non-destructive techniques) were used to check the results from XRD/XRF and examine the structure of inorganic and organic materials in the parchment.

This paper describes the case of a remarkable 15th Century parchment studied mainly with an XRD and XRF portable system. Understanding the materials that constitute graphic works and archival materials facilitates dating, authentication, and comparison with similar documents for the reconstruction of its documental typology, while also helping to better undertake their conservation.

2. Experimental methods

2.1. The privilegio rodado of the Archive of the Royal Chancellery

The document of this study is a *privilegio rodado* (royal solemn privilege). The handwritten privilege, dated to 1459, in which the king Enrique IV of Castile conferred nobility on Gil Fernandez and Alonso Covo (Fig. 1) is one of the most important objects preserved in the Archive of the Royal Chancellery from Southern Spain. The Chancellery was constituted in 1494 – shortly after the conquest of Granada – as the High Court of Justice by Isabel I of Castile and her husband Fernando II of Aragon, the 'Catholic Monarchs'. The document is issued in the form of a quire composed of four sheets of parchment with dimensions 380 × 300 mm. The sheets are written in Castilian with gothic letters on both sides. The ink used for writing is now brownish. The initial capital letter is illuminated with Renaissance themes in reddish pink, green, blue, yellow and black, and gold (Fig. 1a). In the middle of the text on the second sheet, a small coat of arms containing a brown tower is decorated with blue and gold (Fig. 1b).

The main feature of the document is the presence of the royal seal framed by a wheel (*signum regis*) placed in the recto of the last sheet and flanked by a list of witnesses (Fig. 1c). It is this aspect that distinguishes the privileges delivered by the Castilian Chancellery from others dispensed by European governments (Floriano, 1946; Soterraña, 1959). According to the typology established for this type of document (Soterraña, 1959), the *signum regis* matches with model II, which consists of a central circle (with two concentric rings around it) inscribed in a square. Within the central circle is the royal coat of arms of Castile and Lion – two golden castles and two

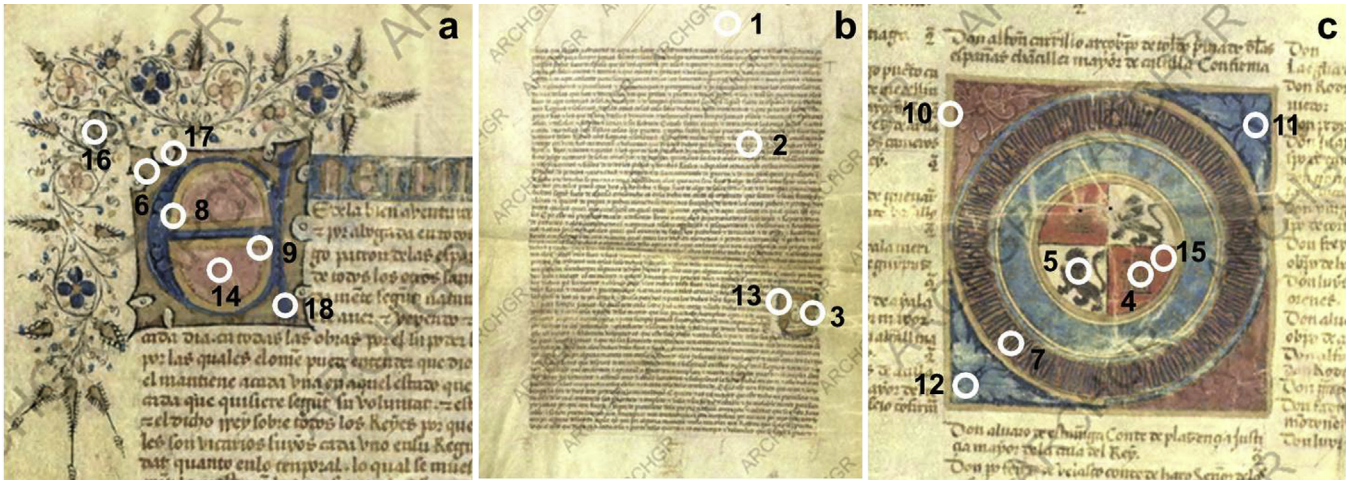

Fig. 1. Areas analysed on the parchment: (**1**) zone without text; (**2**) text area; (**3**) background of the small coat of arms; (**4**) castle in the *rota* of the *signum regis* (gilding); (**5**) lion in the *rota* of the *signum regis* (gilding); (**6**) yellow colour in the capital letter (gilding); (**7**) decorative letters surrounding the *rota* of the seal within the *signum regis* (silvering); (**8** and **9**) yellow colour in two areas of the capital letter; (**10**) yellow colour in the *signum regis*; (**11**) blue colour at the top of the *signum regis*; (**12**) blue colour at the bottom of the *signum regis*; (**13**) blue colour in the background of the small coat of arms; (**14**) reddish pink colour in the capital letter; (**15**) red colour in the base of the castle in the *signum regis*; (**16**) green colour in the capital letter; (**17**) black colour of the drawing in the capital letter; (**18**) blue colour in the capital letter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)