

## Using Solid and Liquid State NMR Techniques to Unveil the Secrets of Ancient Art Pigments

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Organic dyes and their complexes have been used for textiles, manuscript illuminations, paintings and other historic works of art since pre-historic times.<sup>1,2</sup> The most stable reds used in antiquity are based on the 1,2-dihydroxyanthraquinone chromophore, also known as alizarin (highlighted in Figure 1). These dyes were traditionally obtained from the roots of plants belonging to the *Rubiacea* family (madder). In 1868 alizarin became the first natural dye with a known chemical structure synthesised by man. In order to be used as pigments for painting, alizarin extracts must be precipitated in solution with aluminium salts or other inorganic substrates, forming the so-called “lakes” (Figure 1).<sup>3</sup>

Understanding the structure of lakes and the way they bind to the support is essential for a better preservation of art materials. In the past, lake “model” compounds were synthesised using procedures that don’t reproduce the traditional methods, and were characterised by X-ray diffraction,<sup>4</sup> solid and liquid state NMR.<sup>5</sup> In this work, we present a structural comparison between these lakes and others obtained by us following methods more close to traditional ones. Liquid state NMR was used to determine the structural differences between lakes isolated at different pH. <sup>23</sup>Na, <sup>27</sup>Al, <sup>13</sup>C and <sup>1</sup>H NMR gives important information about the structure of the lakes in solid state. In particular, high-resolution <sup>1</sup>H-<sup>27</sup>Al HETCOR (Figure 2) and <sup>27</sup>Al 3QMAS was important to understand the coordination around the aluminium metal in the different complexes.

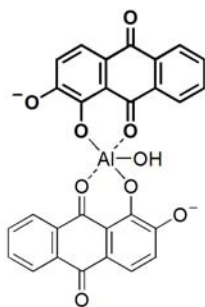


Figure 1

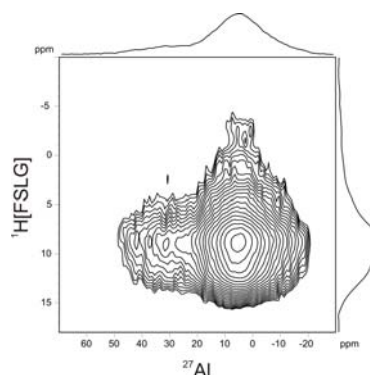


Figure 2

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