Pigments are often present in objects that belong to cultural heritage. Most of them are inorganic and have crystalline phases. Composition of pigments presents characteristic features, because of the ways of extracting raw materials and its specific manufacturing. It is important to have a database of pigment references for helping in the characterization of paintings and answer questions made by art historians or conservators for restoration processes. The pigment references of the National Laboratory of Sciences for Research and Conservation of Cultural Heritage (LANCIC) correspond to pigments from XVI- XVII centuries prepared following historic recipes. They have already been analyzed by other techniques like X-ray Fluorescence (XRF), Raman and infrared (FTIR), but there are some difficulties for non-invasive identification of some pigments. X-ray diffraction (XRD) can overtake these limitations and provide outstanding information for the identification of pigments and the understanding of their preparations. In this work, we present a non-invasive XRD study of this set of pigment references in two ways. The first one in powder and in second step, the same pigments painted on a table using historic recipes. We show the differences between both analyses using two configurations in our XRD-XRF system (called ADIS). Powder analysis of pigments has the small-size configuration (2theta range of: 0-110°); while the non-invasive analysis of the painted table of pigment references has the flat objects configuration (2theta range of: 25 -140°). The painted pigments are mixed with the binder on a ground. There are some preferred orientations in the paintings due to orientation of crystals in the pigment layers. Because of the Cu anode of the system, iron, chrome and cobalt based pigments have a background of fluorescence making difficult the identification. Several paintings have copper based green colors; in this case XRD provides a better identification than other techniques.