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An investigation of the feasibility of applying Raman microscopy for exploring stained glass

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Abstract

Raman microscopy (RM) is widely used in archaeometrical studies of pigments, geomaterials and biomaterials in the Cultural Heritage, but one domain has received relatively less attention: the colouring of stained glass. This feasibility study investigates the advantages and disadvantages of employing RM *alone* in this field by means of a study of modern commercial glasses, modern commercial pigments, and a few archaeological stained glasses, but especially by an experimental project whereby the authors created stained glass. The different kinds of possible unreacted or reacted material are rigorously established. The distinction between Na, K, Ca glasses was explored, as well as the red colouring of an industrial glass which was proved to be due to the presence of (Zn, Cd)S_xSe_{1-x}. Yellow, green, blue and maroon pigments were studied before and after an initial firing and then after heating on glass. The quality of the Raman spectra varied enormously and was sometimes disappointing. Nevertheless RM successfully identified various coloured products such as bindheimite, crocoite, cobalt aluminate, haematite; relict reactants such as corundum, eskolaite and oxides of Co or Pb; and provided indications of other phases such as maghemite or Co-olivine. One conclusion is that the amount of chemical reaction between the pigments and the glass is small compared to the amount in between the pigments. Comments are made on the potential for dating archaeological glass from the known age of synthesis of the pigments, and of the dangers of this approach. Overall it has been shown that RM can be useful for studying stained glass, especially for remote *in situ* analytical operations with mobile RM, but one must expect some problems either with fluorescence or weak spectra.

Keywords: Raman microscopy; Stained glass; Art; Archaeology; Archaeometry; Pigments; Cobalt; Chromium; Eskolaite; Crocoite; Minium; Cadmium; Selenium

1. Introduction

The objective of the present study is to evaluate the capacity, and to demonstrate the efficiency, of non-destructive RM as applied to yet another domain of Art and Archaeology: coloured glass. There exists a considerable literature on archaeometric studies *without* Raman spectroscopy of the physico-chemical nature of historical or modern stained glass from primitive fused beads to exotic cathedral decorations, but mostly in the domains of history and art (e.g. [1–11]) and there is an enormous chemical, physical and geological literature on studies of the *colourless* vitreous state, with or without Raman microscopy (RM) mostly in the domains of physical structures (e.g. SiO_4 rings), chemical compositions (e.g. Li, B, Ge) and thermodynamic properties, but almost all of these works do not include any study by RM of the *colouring* of the glass. Pioneering studies with RM on the colouring in stained glass were introduced by Coupry et al. [12], Macquet [13], Edwards and Tait [14], Smith et al. [15], Bouchard [16] and Bouchard and Smith [17]. Smith and Edwards [18] included "VITRORAMAN" as one of the major domains of "ARCHAEORAMAN" (RM research applications to Archaeology and Art History [19,20]. Numerous text books describe the *physics* of Raman spectroscopy; four recent chapters of books particularly destined for geologists specifically explain the *microscopy* aspect as well as the *mobile* aspect, especially applied to ARCHAEORAMAN domains [20–23]. Bouchard [16] devoted part of a Ph.D. thesis to VITRORAMAN and this paper emanates from that exploratory study on some real historical glass (stained glasses from the XIVth century to the XXth century), some corrosion products on historical glass,

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modern stained glass, today's commercial pigments and also an experimental study carried about by the three authors here. The latter study included analysis of (a) the glass alone; (b) the pigments alone before being applied on the glasses; and (c) the chemical reactions that had occurred between these pigments, the flux and the glass after heating (firing) of the pigments + flux on the glass. In the case of the green and blue pigments there was an extra step in (b): (b′) a mixture of different ingredients; and (b″) firing of this mixture to establish a pre-fabricated pigment of the desired colour.

It is important to mention that it is difficult, if not impossible, to obtain exact information on the chemical compositions of commercial pigments because either the information is withheld at the source or the information provided is incomplete or imprecise. As an example, a commercial pigment labelled "iron oxides" not only did not specify any of the minerals present (and there exists a large number of iron oxy-hydroxides) but the packet also stated "at least 50% of iron oxides"; thus the problem in that case was not so much a question of what are the minor components also present but what are the other major components present. In this connection, in a short parallel study of pigments by scanning electron microscopy various elements like Ti and V were observed although they were not supposed to be present.

The objective here is not to make an exhaustive study on stained glass, but to evaluate the effectiveness and the capacities of RM for the analysis of this type of material and in particular of its colouring. Thus only selected topics on a range of colours are highlighted and the greater part of this paper describes the experimental work from which some deductions were made that may be of use in future studies of historical glass that can now be analysed *in situ* with mobile RM (MRM) [20,23]. A series of Raman spectra of pigments employed in manufacturing stained glass were included in two recent databases of Raman spectra in ARCHAEORAMAN domains [24,25].

2. Analytical conditions

All spectra were acquired with a DILOR® model XY® microspectrometer. After wavenumber calibration using the diamond peak at $1332 \pm 1\ cm^{-1}$, the samples were simply placed in turn in the exciting laser beam under the microscope objective. The Raman spectra were mostly measured with the following operational conditions: red He/Ne laser excitation at 632.8 nm; 30 mW laser power at source reduced considerably by various filters and by the optical trajectory; ×10, ×50 or ×100 objective; 300 μm slits; multichannel CCD detection; integration time 50–400 s and 2–7 accumulations. Green Ar^+ laser radiation at 514.5 nm was also sometimes used with variable but low laser power to reduce heating of the sample. For routine analysis, $\pm 3\ cm^{-1}$ is considered to be the accuracy when comparing spectra from different samples, on different days, or from different instruments; the precision of this apparatus is around $\pm 1\ cm^{-1}$. The spectra presented were sometimes treated by baseline correction and/or minor smoothing.

3. Experimentation

Eight modern commercial glasses of different chemical compositions (Table 1) as well as seven modern commercial pigments (Table 2 lists the five of greater interest) were selected in order to manufacture stained glasses by the method of the surface colouring of glasses. The objective of this experimentation was to investigate by RM which phenomena occur during the heating process as well as to draw up a basic database of the Raman spectra of such pigments and such glasses [15]. In this case, the colouring pigments are metallic oxides which occur as powders (i.e. microcrystals), whether mixed or not. Their application on a vitreous surface followed by one or more heat treatments may lead to chemical reactions and modifications of their Raman spectra (appearances, disappearances, variations in relative intensities, positions and/or widths of the bands).

As in the case of metamorphism of natural rocks or of high *P–T* experimental synthesis of mineral assemblages, there are in principle many events that may or may not happen when, in general, a composite pigment powder composed of mineral pigments plus one or more inorganic fluxes (e.g. silica, SiO_2; minium, Pb_3O_4) is applied to the surface of a glass sheet and is then subjected to one or more heat treatments [15,16]; this may give rise to the existence of several layers or zones, depending on the *P–T–X–t* situation (pressure–temperature–composition–time):

1. A residue of the original powder of composite pigment completely unaltered (normally all blown or scraped away).
2. A residue of the original powder of composite pigment slightly recrystallized (*neocrystallisation* [same structure and same composition] of one or more components which provide some bonding between the components and the glass layer below).

Table 1
Initial compositions of the eight modern glasses that were used to fabricate our experimental stained glasses

Ref.	Potassic flux		Sodic flux					
	"Antique 80110"	"Antique 26"	"Antique 54"	"Antique 73"	"Cordelé"	"Imprimé"	"Ordinaire"	"Antique"
Colour	Red	Yellow	Green	Blue	Uncoloured			
Elements	K, Na, Ca**, Zn, Al*, Se*, Cd*, S**	K, Na, Ba, Zn, Se*, Cd*, Sr*	Na, K, Ca Mg, Al, Cr*, Cu**	Na, Ca, K**, Cu, Mg*	Ca, Na, Mg*, Al**	Na, Ca, Ba, Mg*	Na, Ca, Mg, Al*	Na, Ca, Mg*
Technique	EDX, XRF, PS	EDX, XRF, PS	EDX	EDX	EDX	EDX	EDX	EDX

Underlined: strong proportion; *: small proportion; **: very small proportion. Techniques: EDS electron microscopy (EDX); X-ray fluorescence (XRF); photospectrometry (PS).