



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 $(\text{Zn}, \text{Cd})\text{S}_x\text{Se}_{1-x}$. 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.

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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 ARCHAERAMAN domains [24,25].

2. Analytical conditions

All spectra were acquired with a DILOR[®] model XY[®] microspectrometer. After wavenumber calibration using the diamond peak at $1332 \pm 1 \text{ cm}^{-1}$, 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; $\times 10$, $\times 50$ or $\times 100$ 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, $\pm 3 \text{ cm}^{-1}$ 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 $\pm 1 \text{ cm}^{-1}$. 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, SiO₂; minium, Pb₃O₄) 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	<u>K</u> , Na, Ca**, Zn, Al*, Se*, Cd*, S**	<u>K</u> , Na, Ba, Zn, Se*, Cd*, Sr*	Na, K, Ca Mg, Al, Cr*, Cu**	<u>Na</u> , <u>Ca</u> , K**, Cu, Mg*	Ca, Na, Mg*, Al**	<u>Na</u> , <u>Ca</u> , Ba, Mg*	<u>Na</u> , <u>Ca</u> , Mg, Al*	<u>Na</u> , <u>Ca</u> , 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).

Table 2
Initial compositions of five of the modern pigments that were used to fabricate our experimental stained glasses

Name	"Indicated" chemical composition	Results obtained by RM	X-ray diffraction	Indicated calcination T (°C)
Yellow	"Antimoniate de plomb"	Pb ₂ Sb ₂ O ₇ + PbO (litharge or massicot)	Pb ₂ Sb ₂ O ₇ (bindheimite), PbO (litharge or massicot) + NI	
Green	30 × Cr ₂ O ₃ + 10 × Co ₃ O ₄ + 10 × Pb ₃ O ₄	Cr ₂ O ₃ + PbCrO ₄ /PbCrO ₄ , PbO + PbO + Co ₃ O ₄	Cr ₂ O ₃ , PbCrO ₄ , PbO(?) (litharge) + NI	1100
Blue	"Aluminates de cobalt": 1 × Co ₃ O ₄ + 3 × Al ₂ O ₃	Co ₃ O ₄ /Al ₂ O ₃ + Al ₂ O ₃ + PbCrO ₄	Unidentified	1250
Ordinary black	60 × Fe ₃ O ₄ + 40 × MnO	Alpha-Fe ₂ O ₃ + Mn _x O _y	Alpha-Fe ₂ O ₃ , Fe ₃ O ₄	620
Maroon XVth	"Ordinary black" + zincate de fer + Fe ₂ O ₃	Alpha-Fe ₂ O ₃	alpha-Fe ₂ O ₃ + Fe ₃ O ₄	

Note: all of the pigments included the flux ("fondant rocaillé") in a proportion of approximately 50% by weight. N.I. denotes "not identified" X-ray peaks. Italics denote minor proportions.

- A pigment in which one or more components recrystallized and changed structure (polymorphism) without any chemical reaction with the other minerals or with the glass.
- A pigment in which one or more components reacted chemically with the adjacent minerals, creating new phases (crystalline or glassy), but did not react chemically with glass.
- A pigment in which one or more components reacted with initial glass and created new phases (crystalline or glassy).
- A combination of 4 + 5 whereby a newly-formed phase subsequently reacted with the glass.
- Glass in which one or more components of the original pigment were completely dissolved, colouring the glass in the mass, but without leaving any crystalline traces.
- Glass in which one or more components of the original pigments did not dissolve, or at least not completely, but entered the glass as undissolved or immiscible nanoparticles that coloured the glass in the mass, leaving disseminated crystalline traces.
- A combination of 4 + 8 whereby a newly-formed phase entered the glass creating disseminated crystalline traces
- Glass unaffected chemically by the pigments but internally-restructured by the heating.
- Completely unchanged glass.

Clearly the situation is potentially complex and the recognition by RM of a mineral phase in any glass, historical or not, does not mean that that specific phase had been added to the original colouring powder. An interesting aspect of this classification is the consideration of the formation of reaction products between various components of the pigments + flux without any implication of the glass support. Situations 1 and 2 detailed above should not be observed in our samples because of the gentle scraping carried out after heating in order to eliminate any loose powder remaining on the surface of the glass.

The glasses of recent industrial production were analysed by various techniques in order to obtain their exact elementary composition (Table 1). The analysis of the pigments in or on the glasses used in this study was done by X-ray diffraction and RM; the results obtained by these two methods are presented in Table 2 along with the compositions communicated by the manufacturer. The analysis of chromophoric minerals relates here to the *initial* composition *alone* or to the *mixture* obtained just before the addition of the binder: all of the pigment materials were made up of various oxides mixed with a flux of amorphous silica and minium (5SiO₂ + 4Pb₃O₄, proportion in moles); the mixture was then added to a binder (Arabic gum) before being applied on the glass for heating. In certain cases (green, blue and brown pigments), the pigments were mixed in alcohol and then fired at around 1100–1200 °C; it is only after this operation and a soft crushing that they were mixed with the flux and the binder and applied on the glass for a gentle heating.

Table 3 details the attributions of the various Raman bands of glasses according to their composition (sodic or potassic).

Table 3
 Attributions of the various Raman bands of glasses according to their composition (sodic or potassic)

Wavenumber (cm ⁻¹)	Attribution	Ref.
~80	The “boson” band may be observed at low wavenumbers but it was not observed under our analytical conditions. It corresponds to an excess of diffusion at low frequency and is characteristic of glasses.	[13]
~430	In general under ambient conditions, this very wide band is observed around 430 cm ⁻¹ for a pure SiO ₂ glass (at high pressure this becomes narrower and is shifted towards higher wavenumbers up to ~600 cm ⁻¹).	[52,53]
~[500–600]	This band corresponds to deformation vibrations of the angle Si–O–Si (delta) around bridging oxygens; the number of bands depends upon the angle and hence the nature and the concentration of the neighbouring cation.	[13,52,53]
~[760–1000]	Correspondences with valency vibrations of Si–O	
770	Related to the presence of 2 linked tetrahedra (sorosilicates) (Si ₂ O ₇) ⁶⁻ in sodic glasses.	[13]
790–850	Related to the presence of isolated tetrahedra (nesosilicates (SiO ₄) ⁴⁻ ; group Q ₀), i.e. without bridging oxygens, especially in phospho–potassic glasses.	[50–53]
900–950	Characteristic of group Q ₁ corresponding to tetrahedra with 1 bridging oxygen.	
950–1015	Characteristic of group Q ₂ corresponding to tetrahedra with 2 bridging oxygens.	
1080–1120	Characteristic of group Q ₃ corresponding to tetrahedra with 3 bridging oxygens; this is particularly sensitive to the nature and the concentration of the introduced cation.	
1150–1200	Related to the presence of completely connected tetrahedra (tectosilicates), especially in calcic–sodic glasses.	[50,51]
1084	Consequence of the addition of CO ₂ to the glass and corresponds to symmetrical stretching vibrations of CO ₃ ²⁻ .	[53]
1430 et 1550	Consequence of the addition of CO ₂ to the glass and corresponds to asymmetrical stretching vibrations of CO ₃ ²⁻ (ν ₃).	[52]

4. Results: glasses

4.1. Calcic–sodic glasses

4.1.1. Generalities

Calcic–sodic glasses are represented here by five glasses “*antique*” [un-numbered], “*antique73*”, “*cordelé*”, “*ordinaire*” and “*imprimé*” (Table 1). The attribution of the various Raman bands of these glasses is summarised here. “*Antique*” glasses have been especially manufactured for stained glasses since nearly a hundred years ago; better adapted to this application, they contain more soda and potash compared to ordinary modern glasses which are too rich in silica [26]. In the text the following symbols are used to describe the nature of the Raman bands: L, broad; F, weak; S, strong; the symbols Q₀–Q₃ are described in Table 3 where underlining emphasizes the bands which could be correlated with the described characteristic Raman bands of glass.

4.1.2. “*Antique*” [un-numbered] glass and “*antique 73*” glass

All the identified bands are similar to the traditional Raman bands of sodic glass (bands at 341 (L), 445 (L, F), 570, 788, 1047, 1088 cm⁻¹) (see Table 3). If one can distinguish clearly the Raman bands characteristic of the sorosilicate group (at 788 cm⁻¹) and Q₃ (1088 cm⁻¹), the bands that may be ascribed to the group Q₀ (780–850 cm⁻¹), Q₁ (900 cm⁻¹) and Q₂ (950 cm⁻¹) are unfortunately masked by the parasitic luminescent bands of the Olympus ×50 objective (located at 844*, 898*, 921* cm⁻¹) [16].

4.1.3. “*Ordinary*” and “*imprimé*” glasses

These present rather similar Raman spectra to the previous two types but their intensities are lower.

4.1.4. “*Cordelé*” glass

The Raman spectra of this type of glass are of better quality than those described above. One finds here all the characteristic bands of sodic glass: 341 (L, F), 441 (L, F), 573 (S), 788 (Q₁ sorosilicate group), 947 (Q₂ group), 988 and ~1100 (Q₃ or tectosilicate group), all in cm⁻¹ (Fig. 1).

4.2. Sodic–potassic glasses

4.2.1. Generalities

Sodic–potassic glass here concerns the “*antique54*” glass which presents a quasi-identical proportion of K and Na; however great differences between the Raman spectrum of this glass and that of the calcic–sodic glasses (i.e. “*antique*” [un-numbered] and “*antique 73*”) were not observed.

4.2.2. “*Antique 54*” glass

This glass revealed bands at: 354 (L), 431 (L, F), 568, 785, (*), 1043 and 1080 cm⁻¹. Furukawa et al. [27] presented Raman

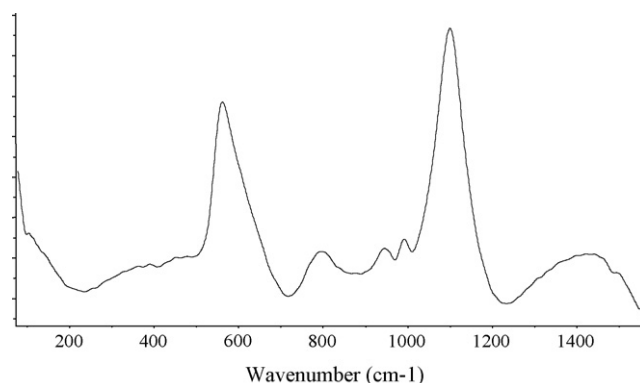


Fig. 1. Raman spectrum of “*cordelé*” glass (file BQCO04). Laser 632.8 nm. Ordinate is the intensity in arbitrary units (also in all other figures).

spectra of polarized glasses of SiO_2 for different concentrations of Na_2O . The large width of the Raman bands of the glasses presented in this article do not permit to make any correspondence with a proportion of oxides by referring to the spectra of Furukawa et al. [27]. However, in the particular case above of the calcic–sodic “cordelé” glass, one can deduce that it has an approximate proportion between $[\text{Na}_2\text{O}, 2\text{SiO}_2]$ and $[\text{Na}_2\text{O}, 2.45\text{SiO}_2]$ (in mol%); this deduction is mainly based on the aspect of the spectra and the position of the band at $\sim 573\text{ cm}^{-1}$ characteristic of the bending deformation of Si–O–Si .

One may also note that the Raman spectra of the three calcic–sodic glasses “antique” [un-numbered], “antique73” and “cordelé” are very close to the spectrum of the calcic–sodic glass presented by Coupry et al. [12] as well as of the spectra of the glasses 8105 and 8104 presented by Macquet [13]. The influence of heat treatments on certain Raman bands of the spectrum of sodic glasses, emphasized by Macquet [13] is quite visible on certain glasses studied in this article. Indeed, glasses used within the framework of this study were subjected (alone or with a layer of pigment) to temperatures that sometimes reached 1260°C . The shifts in wavenumber are more significant in the band theoretically identified at 770 cm^{-1} (band of the sorosilicate group, see Table 3) and observed at $\sim 788\text{ cm}^{-1}$ in the “antique” [un-numbered], “antique73”, “antique54” and “cordelé” glasses. This is also the case of the band calculated at 940 cm^{-1} (Q_1) and observed in cordelé glass around 947 cm^{-1} (Table 3). On the other hand, the theoretical band at 570 cm^{-1} does not seem to be affected by the thermal treatment (Macquet [13] observed a shift of this band towards a lower wavenumber at 560 cm^{-1}).

4.3. Potassic glasses

4.3.1. Generalities

Potassic glasses are represented by the “antique 80110” and “antique 26” coloured glasses.

4.3.2. “Antique 80110” glass

This strong red-coloured glass which is coloured with zinc–selenium–cadmium–sulphur (Zn–Se–Cd–S) (analysed by XRF/EDX), provides a rather spectacular Raman spectrum (bands at 195 (strong), 288 (strong), 391 (weak), 483, 580, 780 cm^{-1}) (Fig. 2). This sort of glass acquires its colour after an adapted heat treatment (thermocolouration). During this thermal process, nanostructures are formed; these were determined to have a composition of the type “ $\text{CdS}_x\text{Se}_{1-x}$ ”. According to the Zn concentration, one can observe, in addition with the first type, other nanocrystallites of the types “ $\text{ZnS}_x\text{Se}_{1-x}$ ” and “ $\text{Zn}_y\text{Cd}_{1-y}\text{Se}$ ” [28]; these last two types are known to create the colour known as “cadmium yellow” probably at the origin of the yellow colouring of the “antique 26” glass studied below. Thus the colour here appears to come from the mineral structure and not from the glass structure. Yu et al. [29] proposed a Raman spectrum of conductors containing $[\text{Zn}, \text{Cd}, \text{Se}]$ and $[\text{ZnSe}]$ but this is not similar to the spectrum obtained on the “antique 80110” glass presented just below. Wang et al. [30] presented, on the other hand, the Raman spectrum of a mixture of Cd and

$\text{Se} \pm \text{Zn}$ with bands at ~ 190 , ~ 290 and $\sim 480\text{ cm}^{-1}$ very close to those of the “antique 80110” glass. Finally, Schreder and Kiefer [31] reproduced the Raman spectra of various glasses containing inclusions of $\text{CdS}_x\text{Se}_{1-x}$ with various proportions of S (Fig. 2); these spectra thus enable us to correlate very well the Raman spectrum of the “antique 80110” glass with a $(\text{Zn}, \text{Cd})\text{S}_x\text{Se}_{1-x}$ bearing glass containing a proportion of about 45 at.% of S or (S + Se). Schreder and Kiefer [31] mentioned that the Raman bands allotted to the LO and TO bands of CdSe are replaced by respectively the LO and TO bands of ZnSe in the case of material containing (Cd, Zn)Se.

The recognition of $(\text{Zn}, \text{Cd})\text{S}_x\text{Se}_{1-x}$ in this glass potentially has a considerable significance. Any mineral oxide pigment (or even a non-oxide) that is completely dissolved in any glass can, by definition, no longer possess its original crystal structure and hence cannot still give the relevant original Raman spectrum as the atoms are dispersed in a semi-amorphous matrix. The fact that we can identify $(\text{Zn}, \text{Cd})\text{S}_x\text{Se}_{1-x}$ implies either that they are real crystallites existing as nanocrystals (nano-sized

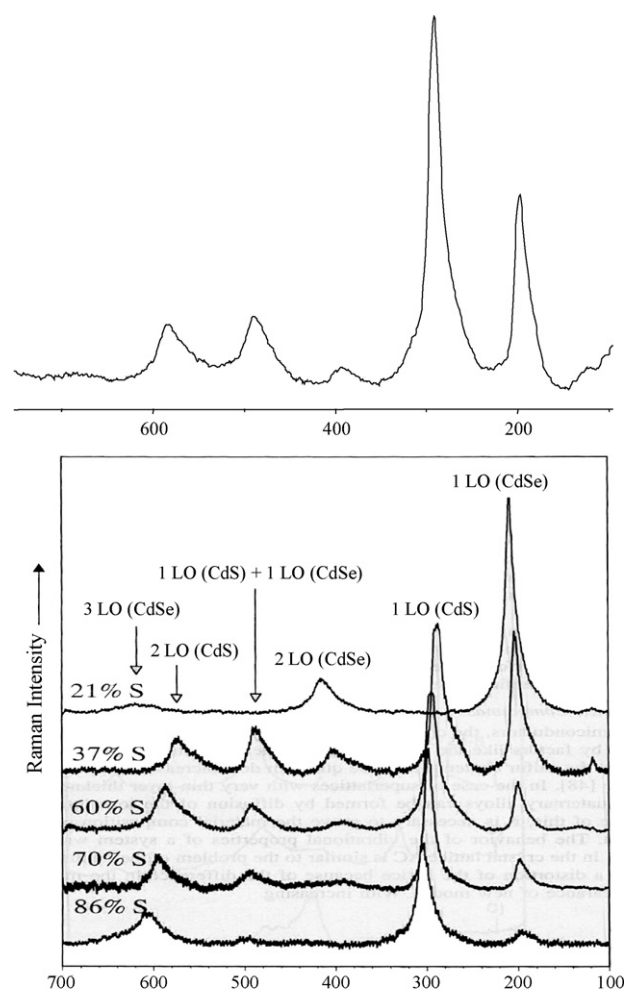


Fig. 2. Raman spectra of nanocrystals of $\text{CdS}_x\text{Se}_{1-x}$ in a glass matrix (bottom) (modified after [31]) with our Raman spectrum of “antique 80110” glass (top: file BUVE07; laser 632.8 nm). Note that our Raman spectrum of “antique 80110” glass is exceptionally presented with a reversed horizontal scale in order to facilitate the superposed comparison (both in cm^{-1}).

because they are not observable with a high-power microscope) or the Raman spectral details reveal chemical bonds between Zn, Cd, S and/or Se with Si and O of the glass, or of Si–O vibrations modified by adjacent Zn, Cd, S and/or Se. Thus there may be a co-existence of mineral particles and true glass that is effectively a simple case of immiscibility between silicate and sulphide/selenide.

4.3.3. “Antique 26” glass

This yellow-coloured potassic glass unfortunately does not provide any exploitable Raman spectrum because of its intense fluorescence. The negligible quantities of Sr and Ba recorded by XRF should not fluoresce. This fluorescence is probably due to the nanocrystallites (Zn–Cd–Se–S) described above. The colouring of glasses with Zn–Cd–Se–S can be very variable: from lemon-yellow to dark-red according to the ratio between SeCO_3 and CdCO_3 incorporated in the mix before vitrification [28]. The importance of ZnO is not yet well known; indeed according to certain authors, glasses with strong Zn content are coloured in red, but according to others it is those that do not contain Zn which are the reddest!

5. Results: pigments

5.1. Yellow pigment alone (after firing)

The analysis of the yellow pigment by RM provided a spectrum of bindheimite, $\text{Pb}_2\text{Sb}_2\text{O}_7$, more commonly called “Naples yellow” by artists and art historians, or lead(II) antimonate by chemists [16]. This phase was previously identified by RM by Bell et al. [32] as having Raman bands at 140, (*), ~ 329 , (*), 448, (*) ((*) cm^{-1} wavenumbers deduced from the published spectrum but not listed in the text by the authors, *denotes a wide imprecise position). This mineral pigment is also mentioned by Colomban [33] as being a yellow colouring pigment frequently observed on certain ceramics. It is mainly identified here by the following Raman bands: 145(?), 200, 285(?), 318, 336(?), 449, 508, 599, 702, 960 where the Raman bands annotated with (?) can also be allotted to tetragonal PbO (litharge). This result corresponds perfectly to the denomination given by the supplier (see Table 2) as well as to the results by X-ray diffraction analysis by ourselves (bindheimite predominant + PbO). Clark et al. [34] indicates a date of the first synthesis or manufacture of this mineral pigment around 1570–1293 B.C. in ancient Egypt.

5.2. Yellow pigment after heating on glass

The Raman spectra of the yellow pigment on glass, compared with spectra of the yellow pigment alone, do not provide any trace of reaction between the pigment and glass. The acquired spectra are similar in all points and are presented in Fig. 3.

5.3. Green pigment

5.3.1. Generalities

An analysis of the initial products having been used to manufacture the green pigment was carried out. These include in

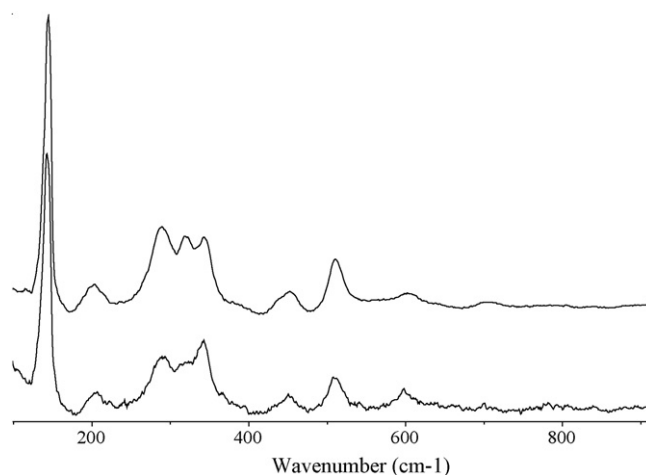


Fig. 3. Raman spectra of the yellow pigment alone (lower: file BVJA06) and this applied and heated on the “cordelé” glass (upper: file BVJA03). Laser 632.8 nm.

particular eskolaite (Cr_2O_3), minium (Pb_3O_4) and cobalt oxide (Co_xO_y) [16]. Table 4 summarises the results obtained on the basic components of the green pigment with comparisons of the existing data in the literature [32,35–39].

The industrial production of chromium oxide had begun in Europe only around the beginning of the XIXth century [33]; the identification of this mineral in pigments has consequently become an extremely tempting mode of relative dating. However there is a great danger in this approach. If “modern” science did not know how to extract or to synthesise a certain pigment, such as anatase [40] or lazurite . . . , until some relatively recent time (one often cites the period 1850–1950), it would be necessary to prove that in ancient times the craftsmen of the day had not already manufactured it or learned how to extract it from some natural geological, vegetal or animal material.

The analysis by RM of the green pigment after firing delivered interesting results. Its Raman spectrum is in total agreement with the results obtained by X-ray diffraction, the composition provided by the manufacturer as well as the data in literature. Some other chromium products were already identified by RM [32,36–37]. Table 5 gathers the various results of these authors, those obtained on the green pigment after firing as well as the results obtained after the application and heating on the glass support. In addition to the three products described above and in Table 4, Raman spectra of products of the complexation of chromium with alkalis, halides or other metals (ex: K_2CrO_4 , HCrO_4^- , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$, MnCr_2O_4 , FeCr_2O_4 , CrCl_3 , CrCl_2 , . . .) are also described by Abourazouk [37].

5.3.2. Green pigment alone (after firing)

In the Raman bands of the green pigment alone after firing there is a good correspondence with the bands of crocoite (PbCrO_4) or the phase $\text{PbCrO}_4\cdot\text{PbO}$ for four bands in the zone $336\text{--}403\text{ cm}^{-1}$ along with the very strong band at 839 cm^{-1} (Table 4, Fig. 5). These correspond to the product of the heating reaction between eskolaite (Cr_2O_3) and minium (Pb_3O_4) during

Table 4

Raman data obtained on the different initial pre-firing materials of the green pigment compared to data in the literature

Ref.	Eskolaite, Cr ₂ O ₃ , Raman bands (cm ⁻¹)								
TW, FBVI3		305	347				550	607	
[36]							551	614	
[32]	221	308	349				552	611	
[35]		303	351	397	530		551	609	
[37]		300	350	397	530		550	610	
Ref.	Co _x O _y , Raman bands (cm ⁻¹)								
TW, FBVI5 and FUCO3		193	478				682		
[38] "Co ₃ O ₄ + CoO"		192	465	511			604	667	
Ref.	Minium, Pb ₃ O ₄ , Raman bands (cm ⁻¹)								
TW, FQVI4	51, 60, 70, 84	120	150	223	313		391*	480	549
[32]		122	149	223	313	340#	390	480	548
[23]	32, 53, 64, 71, 86	121	151	223	314		391	481	550

TW: this work, the following code number gives the spectrum number; 340#: band considered to belong to litharge; (*) very weak band.

Table 5

Raman data obtained on chromium-bearing materials on the green pigment after addition of the flux and firing^a and after heating on the glass^b, and archaeological 19th century stained glass (sample A3, Strasbourg, France)^c compared with data from the literature^d

Ref.	Species	Raman bands (cm ⁻¹)								
TW ^a , BQGR02	Green pigment after firing	138	196*	337	357	376	*	515*	552*	
TW ^b , BUVE04	Green pigment on glass	142	194	322	339	353	379	401	478	514
TW ^c , CFVE03	Green pigment on sample A3	139	191	*	338	*	*	*	547	601
[37] ^s	KCrO ₄ ⁻					350				
[37] ^s	HCrO ₄ ⁻			323		347				
[37] ^s	CrO ₃									
[35] ^s	Cr ₂ O ₃		303	351	397			530	551	609
[32] ^s	Cr ₂ O ₃ ·2H ₂ O		266					487	552	585
[42] ^s	Ca ₃ Cr ₂ Si ₃ O ₁₂ (uvarovite, non-stoichiometric)	176	214, 240	322	338	368	399		510, 530	560
[37] ^s	Cr(OH) ₃							530		
[36] ^s	Cr(OH) ₃							524		
[36] ^s	CrO ₄ ²⁻									
[32] ^s	PbCrO ₄			338	360	372	403			
[32] ^s	PbCrO ₄ ·PbO			336	358	374	401			
Ref.	Species	Raman bands (cm ⁻¹)								
TW ^a , BQGR02	Green pigment after firing					839				
TW ^b , BUVE04	Green pigment on glass			824		836		845	926*	
TW ^c , CFVE03	Green pigment on archaeological sample A3			826		835		843		1317, 1655*
[37] ^s	KCrO ₄ ⁻							845		
[37] ^s	HCrO ₄ ⁻								880, 953	
[37] ^s	CrO ₃								880, 975, 1006	
[35] ^s	Cr ₂ O ₃									
[32] ^s	Cr ₂ O ₃ ·2H ₂ O									
[42] ^s	Ca ₃ Cr ₂ Si ₃ O ₁₂ (uvarovite, non-stoichiometric)					840			894, 1004	
[37] ^s	Cr(OH) ₃									
[36] ^s	Cr(OH) ₃								3490	
[36] ^s	CrO ₄ ²⁻					840				
[32] ^s	PbCrO ₄					841				
[32] ^s	PbCrO ₄ ·PbO					838				

Refs.: TW, this work; the following code number gives the spectrum number; (*) very weak band.

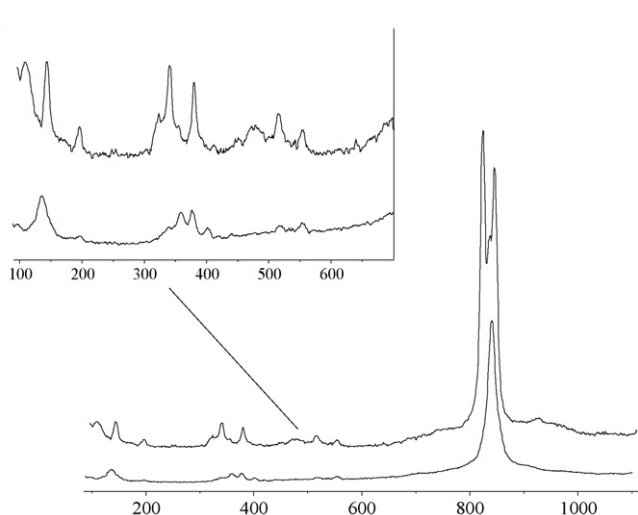
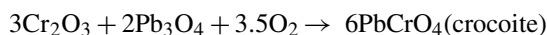


Fig. 4. Raman spectra of the green pigment alone (lower: file BQGR02) and the green pigment on “cordelé” glass (upper: file BUVE04); at the top left is an enlargement of both. Laser 514.5 nm.

the firing of the mixture (Cr₂O₃ + Pb₃O₄ + cobalt oxide Co_xO_y). In the presence of oxygen the following reaction occurs:



PbCrO₄-PbO type compounds can also result from a similar reaction with more Pb₃O₄ and less O [32]. Crocoite alone is orange (and minium is pink) such that the green colour of eskolaite is lost; hence the overall green of the fired pigment would come from a mixture of the orange crocoite and the blue cobalt oxide (by colour subtraction/absorption), unless there is a *substantial* residue of eskolaite; however, if it is certain that cobalt oxide has a determining role in the green colouring of this pigment its chemical implication during the firing is not yet well defined. The Raman bands located at ~196 and ~515 cm⁻¹ (spectra BQGR02 and BUVE04 in Table 5) cannot be allotted to any known species of a chromium complex, but they are very close to the characteristic bands of the blue pigment made up mainly of cobalt aluminate (201, 512, 841 cm⁻¹) (see below and Table 6). The band at 552 cm⁻¹ (Table 5), of very low intensity, corresponds to the band of eskolaite (and also to Cr₂O₃·2H₂O but this should not exist after firing) and hence reveals the presence of *some* of this reagent in the final reaction product after the firing. Lastly, the Raman band at 138 cm⁻¹ (Table 5), also absent from all the products of chromium presented above, is very probably derived from a lead oxide, whether or not complexed with the final product (i.e. PbO (massicot): 143 cm⁻¹; PbO (litharge): 145 cm⁻¹). The X-ray diffraction pattern of this pigment presents a great multiplicity of bands making the interpretation therefore more complex. The pattern nevertheless permits to confirm the presence of eskolaite and of crocoite, but several other bands remain unallocated (Table 5).

Some bands of the green garnet uvarovite correspond with the spectrum of Fig. 4 (upper) and garnets are characterised by two strong bands in the 815–925 cm⁻¹ spectral zone [41,42]; however uvarovite can be excluded since garnet was not found in the original components and calcium was not added, but this

Table 6
Raman data obtained on the different constituent products of the blue pigment, compared with literature data

Ref.	Species	Raman bands (cm ⁻¹)
[43]	Corundum, Al ₂ O ₃	378
[41]	Corundum, Al ₂ O ₃	380
[41]	Al ₂ SiO ₄ (OH,F) ₂	159*, 171, 198, 242, 271, 288, 313, 335, 363, 405, 462, 553, 843, 925, 978*, 997, 1114, 1166
[41]	Al ₂ SiO ₅ andalusite	292, 322, 360, 552, 920, 951, 1021, 1065
[41]	Al ₂ SiO ₅ kyanite	300*, 324, 360, 391, 403, 438*, 448, 485, 563*, 571, 637, 672, 704, 725, 890, 954, 1004
[41]	Al ₂ SiO ₅ sillimanite	142, 239, 316, 397, 431, 467, 491, 604, 714, 878, 919, 973, 1045, 1140
Ref.	Species	Raman bands (cm ⁻¹)
TW, BTBL02	Blue pigment (alone)	201
[38] "Co ₃ O ₄ + CoO"		412*
[32] CoO·Al ₂ O ₃		192
		203
		~512
		511
		512
Ref.	Species	Raman bands (cm ⁻¹)
TW, BTBL02	Blue pigment (alone)	201
TW, BTBL12	Blue pigment (on glass)	205
TW, DNV102	Blue pigment on sample M4	205
[32]	CoO·Al ₂ O ₃	203
[32]	CoO- <i>n</i> SiO ₂ (smalt)	462
		412*
		413*
		338*
		378*
		604, 667
		~512
		515
		515
		512
		841*
		841
		839
		827
		841*
		919
		920

Refs.: TW, this work; the following code number gives the spectrum number; (*) very weak band.

demonstrates the difficulty of interpreting Raman spectra when major bands correspond as well as some minor ones, bearing in mind that garnet is a solid-solution and most of the bands shift with chemical composition [43].

5.3.3. Green pigment after heating on glass

Comparison of this pigment on the surface of the glass (Table 5, Fig. 4) reveals certain changes with respect to the spectrum of the pigment alone after firing (Table 5, Fig. 4) and hence also with the initial components (Table 4). At small wavenumbers ($<600\text{ cm}^{-1}$), there are no major modifications, but around 850 cm^{-1} certain significant dissimilarities are observed on the glass. The green pigment alone gave a single very strong Raman band at 840 cm^{-1} deduced to be due to a Pb chromate/oxide structure whereas the spectrum of the pigment on glass provides three distinct Raman bands, located at 826 , 836 and 844 cm^{-1} , with different relative intensities according to which spectrum. Moreover, a very low intensity band at $\sim 926\text{ cm}^{-1}$ appears in addition (however one must bear in mind that this last band, as well as that at 844 cm^{-1} , also corresponds to three parasitic bands of the Olympus objective, located in this same zone of wavenumbers: 844 , 895 , 921 cm^{-1}) [16,22].

Table 5 summarises the various Raman bands identified on the green pigment alone after firing and on the green pigment on glass as well as providing a comparison with bands in the literature concerning different chromium-bearing materials. Certain bands not observed on the spectrum of the green pigment alone appear in the spectrum of the green pigment on glass. These include the bands at 322 cm^{-1} (assignable to a HCrO_4^- complex), 478 , 824 and 836 cm^{-1} (all not yet all allocated) and 845 cm^{-1} (assignable to a KCrO_4^- complex). The bands situ-

ated at 322 and 845 cm^{-1} correspond to a complexation between the CrO_4^{2-} anions with respectively the cations coming from previous dissolved water or from the atmospheric environment (H^+) and from the glass (alkali: K^+). It is highly probable that the bands at 824 cm^{-1} and 836 cm^{-1} also correspond to complexes with the chromate anion CrO_4^{2-} and of cations of the same or similar type. One may note the stronger intensity of the Raman bands (with the same analytical instrumental conditions) with the green pigment on glass compared with the green pigment alone (Fig. 4); this is probably due to the effect of heat diffusion favoured by a more compact mixture and by the glass support compared to a powder, notorious for poor heat diffusion.

5.3.4. Green pigment on archaeological glass

A fragment of stained glass labelled "A3" (from Strasbourg, XIXth century) provides a spectrum (Table 5, Fig. 5) very similar to the one obtained on the green pigment applied on modern glass. Many of these Raman bands can be attributed as follows to chromium complexes and their reactions with lead, as it was shown above in the case of the modern stained glass:

- Pb in PbO form (139 cm^{-1});
- cobalt aluminate (191 cm^{-1});
- HCrO_4^- (around 322 cm^{-1}),
- crocoite (338 , around 353 , around 379 , 835 cm^{-1});
- possibly traces of eskolaite Cr_2O_3 or $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (547 cm^{-1});
- KCrO_4^- (843 cm^{-1}), or the Olympus parasite;
- non-identified bands (around 478 , 826 cm^{-1} , but also occasionally found in archaeological and experimental pigment which contain Cr and Co);

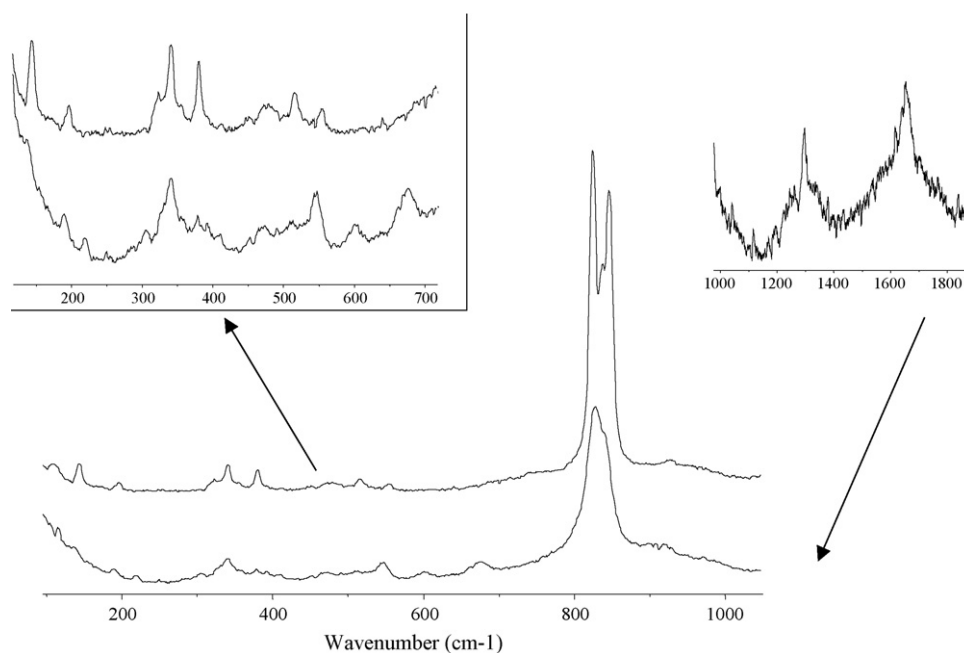


Fig. 5. Raman spectrum of the green pigment on "cordelé" glass used for our modern stained glass (upper: cf. Fig. 4), and the Raman spectrum of the pigment on the archaeological stained glass "A3" (lower: file CFVE03); top left is an enlargement of both; the top right inset shows the additional Raman bands at 1317 and 1655 cm^{-1} observed on the archaeological pigment. Laser 514.5 nm .

- certain bands of low intensity, not allocated (601 , 677 , 1317 and 1655 cm^{-1}) and presumably belonging to one or more additional phases.

It may thus be deduced that in the archaeological glass the green colour is again derived from the influence of the blue from cobalt aluminate and the orange of crocoite and that the starting materials were most probably the oxides of Al, Co, Cr and Pb with a flux made of the oxides of Pb and Si; the non-identified bands indicate yet further products and hence further starting materials (or impurities in the mentioned ones).

5.4. Blue pigment

5.4.1. Blue pigment alone (after firing)

Perhaps there are non-indicated basic components in addition to ($\text{Co}_3\text{O}_4 + \text{Al}_2\text{O}_3$), that have been used for the commercial manufacture of the blue pigment, but in any case the analysis of the final product corresponds very well to the expected heated product: cobalt aluminate ($\text{CoO}\cdot n\text{Al}_2\text{O}_3$) also named “cobalt blue” and resulting from a firing reaction at more than 1000°C between the essential basic components mentioned above. Table 6 shows the Raman bands identified in the literature for corundum (alpha- Al_2O_3) (in general of weak Raman response) that enter partially in the composition of the blue pigment [41,44] along with data on Al_2SiO_5 and cobalt oxide, aluminate and silicate. The weak band at around 412 cm^{-1} may well represent a residue of corundum.

The poor existing Raman data on cobalt oxides, which are very rare and inexistent in a natural state, does not enable us here to define exactly which exact mineral species are present, nor to know if the cobalt oxide is in solid-solution with another element such nickel or zinc as mentioned by Bachmann [45]. The spectrum obtained on the blue pigment is however very similar to that of cobalt aluminate identified by Bell et al. [32] and Chen et al. [38] (Table 6) and the bands at around 196 and around 512 cm^{-1} correspond to the deduced cobalt aluminate in the green pigment (Table 5). Colomban [33] quotes “ CoAlO_4 ” spinel obtained by the reaction between cobalt oxide et Al_2O_3 , whereas Bachmann [45] gives the correct formula CoAl_2O_4 for a spinel (XY_2O_4). In any case the Raman bands observed do not correspond to the bands of this spinel, and the two weak bands with 841 and 919 cm^{-1} correspond to the parasitic bands of the Olympus $\times 50$ objective [16]. Likewise by X-ray diffraction analysis there is little data on various cobalt oxides. Indeed, the XRD patterns obtained on the blue pigment cannot for the moment be correlated with any known cobalt species already indexed in ASTM or JCPDS identification databases.

5.4.2. Blue pigment after heating on glass

Cobalt aluminate figures as a key component as expected, and again the weak band at around 413 cm^{-1} may well represent a residue of corundum. Certain new bands not observed on the spectrum of the blue pigment alone (or of very weak intensity) appear at the wavenumbers at: 338 , 378 , 827 and 841 cm^{-1} . These do not correspond to the traditional species of $\text{CoO}\cdot\text{Al}_2\text{O}_3$

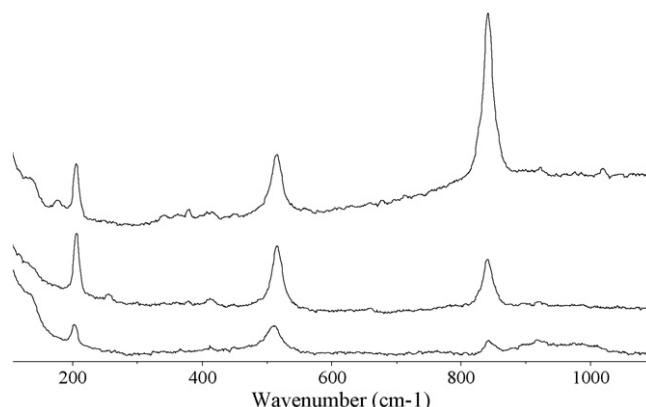


Fig. 6. Raman spectra: the blue pigment alone (lower: file BTBL02); on “imprimé” glass (middle: file BTBL07), and on “antique 73” glass (upper: file BTBL12). Laser 514.5 nm .

observed for the blue pigment alone and described by Bell et al. [32] (these authors indicate a date of 1775 for the beginning of the manufacture of this pigment). The bands at 338 and 378 cm^{-1} being of very low intensity cannot be allotted to a mineral species with certainty. Nevertheless, it is interesting to note the similarity with the position of certain bands of crocoite at 338 , 372 cm^{-1} [32]. This observation supposes the presence of Cr in the pigment mixture (not announced in the manufacturer’s composition). The intense band at 841 cm^{-1} and its shoulder at 827 cm^{-1} do not correspond any more to the parasite bands of the Olympus objective (cf. above for the blue pigment alone), but seem to correspond to the structure of the blue pigment or to its reaction with the vitreous support (Fig. 6). This last observation is reinforced by the work of Colomban [33] who observed also a band at 822 cm^{-1} in the blue pigment, and who suggested that it corresponds to a mineral species with an “olivine type” structure: Co_2SiO_4 . Natural olivine ($\text{Mg, Fe})\text{SiO}_4$ is characterised by a strong doublet Raman band around 840 cm^{-1} [41] such that an olivine structure is highly credible as one would expect a slightly lower wavenumber when Co replaces Mg. Lastly, the band at 920 cm^{-1} , of very low intensity, could correspond to the formation of a complex (“smalt”) between Co and the silica of glass or the flux ($\text{CoO}\cdot n\text{SiO}_2$) [32], but could also correspond, considering its intensity, to the parasite of the Olympus. Given these results, one can conclude with confidence the existence of at least one reaction between the blue pigment and SiO_2 (olivine formation) but one cannot distinguish between the SiO_2 source being the flux or the glass.

5.4.3. Blue pigment on archaeological glass

Many works have been published on the uses of cobalt since the end of the XIIth century until the end of the XVIIIth century, e.g. [46,47]. Bachmann [45] described the origin of the use of cobalt as a blue pigment during the XVIIIth Egyptian dynasty (1389–1379 B.C.) and shows how various mineralogical compounds react together during the heating to give a final product of spinel type: $\text{CoO}\cdot\text{Al}_2\text{O}_3$ or CoAl_2O_4 (to be related, according to that author to the “cobaltic” form of gahnite that exists in the natural state: ZnAl_2O_4). The presence of cobalt in a XIXth century stained glass fragment (sample M4 from Le Mans) has

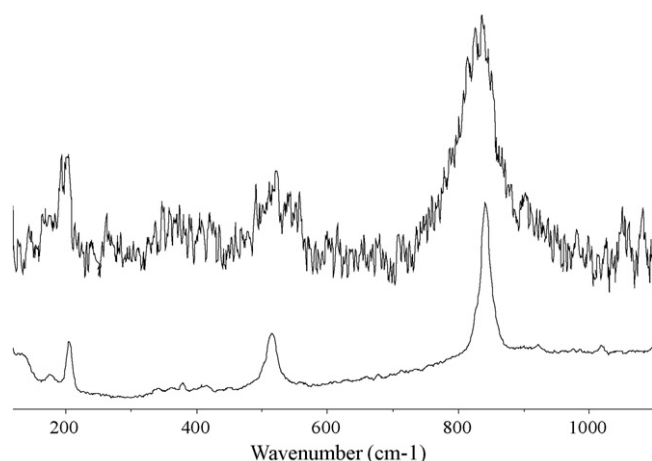


Fig. 7. Raman spectra of the blue modern pigment (lower: file BTBL12), and of the pigment identified on the archaeological stained glass “M4” (upper: file DNV102). Laser 514.5 nm.

been recognised by RM (Table 6, Fig. 7). The two bands quite characteristic of cobalt aluminate, ~ 200 and 515 cm^{-1} , and of Co-olivine, around 830 cm^{-1} , are also present in the spectrum of the archaeological stained glass and thus confirms the presence of these species of cobalt on the glass.

5.5. Maroon pigment (after firing)

5.5.1. Maroon pigment alone

The opacity of the components of this pigment is a source of complication for the analysis by RM (laser absorption, overheating, less light left for the Raman effect). The initial composition of the pigment provided by the manufacturer, without taking account of the (unknown) proportions, is: magnetite (Fe_3O_4), iron zincate, hematite (Fe_2O_3) and manganese oxide (Mn_xO_y) (Tables 2 and 7). The mixture was diluted, fired and crushed, as for the green and blue pigments. The analyses by RM lead only to the identification of heated [16,48] hematite (probably during the firings undergone by the pigment). It may be noted however that, neither magnetite nor iron zincate were observed after the firing ($>1000\text{ }^\circ\text{C}$), such that at this stage, probably only strongly oxidized Mn, Fe and Zn oxides existed.

In general the powdered nature of microcrystalline pigments is basically unfavourable to analysis by RM. It is indeed the very small size of the crystals that incites a local heating effect and an incapacity for adequate heat diffusion to the totality of the sample. This phenomenon results in slight modifications such as a partial heating of hematite [16,48]. Analyses carried out on the “pigments on glass” make it possible to acquire spectra of better quality because the contact between the glass and the pigment

(compacted by heating and some mineral reactions) makes it possible to better diffuse the heat of the laser and thus reduce local heating).

5.5.2. Maroon pigment after heating on glass

RM did not allow recognition of the presence of “iron zincate” as mentioned in the composition transmitted by the stained glass manufacturer. The results however make it possible to distinguish the presence of hematite, certain magnetite traces (characterized by its specific band at $\sim 655\text{ cm}^{-1}$), as well as traces of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (presence of a band at 355 cm^{-1}).

6. Discussion and conclusions

The study on the glasses alone reveals that (i) the study of coloured and uncoloured glasses in a stained-glass project can, as was half-expected, be hampered by either weak Raman spectra or intense fluorescence/luminescence; (ii) in certain cases one can with confidence identify the colorant (e.g. $(\text{Zn}, \text{Cd})\text{S}_x\text{Se}_{1-x}$; and (iii) certain bands involving bonds of Si with bridging or non-bridging oxygens influenced by neighbouring Na can help to determine an estimated proportion of sodium in the glass [27]. The situation is less clear with calcium and potassium such that their presence is largely deduced by the weakness of features attributed to sodium.

The study of the modern glass also made it possible to clearly distinguish the various Raman bands allotted to the various polymerised silicate groups (types Q_0 , Q_1 , Q_2 and Q_3) formed during the depolymerization of the siliceous network by various fluxes.

The restriction to five types of pigments or dyes might appear small since one distinguishes today more than 14.000 nuances of possible colourings, but many of these are organic and would disintegrate on heating. However, the choice made in this study was of inorganic pigments respecting the historical recipes used since the Middle Ages and thus more likely to be identified on archaeological stained glasses (e.g. pigments containing chromium, cobalt, iron or antimony). It should also be considered that, whatever the analytical technique used, the result of the study relates to the current composition of the glass or the pigment and not to the original composition. Indeed both the glass and the pigment materials have been subjected to grinding, mixing and firing, often several times and at different temperatures, and also they have been subjected to various climatic deteriorations with time, especially for archaeological glass. Climatic alteration products have not been introduced above but it is relevant to mention that mineral species such as gypsum or calcite were easily characterised in damaged archaeological stained glasses from the XIIIth to the XIXth century in a related study [16].

Table 7
Raman data obtained on the experimental maroon pigment on glass

Ref.	Species	Raman bands (cm^{-1})								
TW, BYMA5	Maroon pigment on glass: haematite + magnetite	226	246	293	299		412		613	655
TW, CYMA3	Maroon pigment on glass: haematite + magnetite + maghemite	226	246	293	299	355	412	498	613	*

Refs.: TW, this work; the following code number gives the spectrum number; (*) very weak band.

This RM feasibility study of the stained glasses has made it possible to draw certain encouraging conclusions. For example, complexes resulting from the reaction by heating between various minerals of a mixture of pigments could be recognised. Thus the mineral crocoite (PbCrO_4), resulting from the reaction by heating the mixture eskolaite (Cr_2O_3) + minium (Pb_3O_4) could be identified in the green pigment alone and on green experimental and archaeological stained glass. It is also the case of Co-olivine (Co_2SiO_4) derived from the reaction between Co-oxide and the silica of the flux or the glass identified in the blue pigment alone and on blue experimental and archaeological stained glass. On the other hand, certain unreacted initial components subsisted in several cases (e.g. corundum, eskolaite, litharge or massicot). On the contrary, no minium was detected in the pigments on glass implying that it had completely reacted or dissolved in the flux.

It was highlighted that modern commercial pigments often contain many impurities, and often in considerable quantities; one can imagine that older and especially ancient pigments were even less pure. The craftsmen were no doubt not very concerned about this unsatisfactory situation as their objective was to make a desired colour. In our case the presence of probable Cr in the blue pigment on glass could be an impurity, but this did not matter as the dominant intense blue colour from Co could hide any minor effect from Cr. On the other hand in the green pigment on glass, the green colour was not caused by an abundant Cr phase, but by a colour subtraction phenomenon with orange crocoite and blue cobalt aluminate such that Co was an essential and not a minor or impurity component.

Concerning mineral reactions, this RM and XRD study has not recognised *any* new mineral phase containing K, Na or Ca (except tentative KCrO_4^-) that might have migrated out of the glass into the pigment cover, nor a glass structure containing dissolved Co, Cr, Fe, Mn, Pb or Sb. This could mean that (i) such phases give weak Raman spectra, or (ii) they exist in only small quantities, or (iii) that they do not exist. The last two points lead to the hypothesis that the amount of chemical reaction between the pigment (+flux) and the glass is small compared to the amount in between the pigments (+flux). Concerning the flux which was added to promote reaction between phases, it no doubt acted to consolidate everything in order to transform a loose powder into a resistant coloured adhering layer, and its components reacted with the pigment (e.g. minium with eskolaite to make crocoite and SiO_2 with cobalt oxide to make Co-olivine). This study did not recognise any flux-derived glass; presumably this melted flux partly exists between the mineral grains in the reacted pigment and is partly united with the initial glass substrate. Furthermore, analysis of the pigments on glass did not reveal any indications of Na or K-bearing glass such that the Raman signal was essentially derived from the surface pigment layer which is partly or totally opaque. Of course some of these questions could be clarified by employing other techniques, but that was not the objective of this study which was to learn what can be deduced from stained glass by RM employed *alone*.

Lastly, one can mention the exciting potential of relative dating which, thanks to the identification by RM of the chromogenic products, makes it possible to estimate the date of manufacture

of the analysed stained glass. Thus for example the development of the use of lead antimonate ($\text{Pb}_2\text{Sb}_2\text{O}_7$) between 1700 and 1850, of lead chromate (PbCrO_4) since 1800, and of cadmium sulphide (CdS) or “cobalt yellow” ($\text{K}_3[\text{Co}(\text{NO}_2)_6]$) since 1850 [34] may all be considered recent with respect to massicot (PbO) attested as starting from 1070 to 1030 B.C. and realgar (Ag_2S_3) starting from 1550 to 1070 B.C. [49]. Nevertheless, as discussed above concerning the white pigment anatase of recent manufacture but well-known in rocks hundreds of millions of years old, and concerning another well-known pigment in art work namely lazurite (also called ultramarine) of XXth century industrial production but often recorded in Ancient Egypt (as the major component of the rock “lapis lazuli”), it is scientifically difficult to exclude the possibility that more ancient craftsmen used natural minerals analogous to modern syntheses. Thus for example since crocoite is a natural mineral, it is possible that a craftsman somewhere, sometime, used natural crocoite rather than manufacturing it from Pb and Cr oxides. Indeed when one considers that the International Mineral Association has strict rules on mineral names that can only be applied to naturally-occurring phases, then *all* pigments with proper names could have had a natural source that was in fact used well before human activity had found a way of manufacturing it.

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References

- [1] R.G. Newton, *The deterioration and Conservation of Painted Glass: A Critical Bibliography and Three Research Papers*, Oxford Univ. Press, London, 1974, pp. 86.
- [2] J.M. Bettembourg, *Verres et Refractaires* 30-1 (1976) 36.
- [3] J.M. Bettembourg, ICOMOS, in: 10th General Assembly, Sri Lanka, E. Bacher (Ed.), 1993, pp. 195–202.
- [4] J.M. Bettembourg, *Analisis* (Paris) 19-6 (1991) 43.
- [5] J.M. Bettembourg, in: *Les arts du verre: Congress Proceedings*, Namur, France, 1991, pp. 111–117.
- [6] A. Winter, *Verres et Refractaires* 36-1 (1982).
- [7] G. Libourel, P. Barbey, E.-M. Chaussidon, *La Recherche* 25–262 (1994) 168.
- [8] A. Salem, *Glass Technol.* 35-3 (1994) 135.
- [9] A. Orlando, *Analyst* 121-4 (1996) 553.
- [10] M. Verita, in: *Dossier de la commission royale des monuments, sites et fouilles*, Belgium, Liège, 1996, pp. 61–68.
- [11] J. Sterpenich, *Techné* 6 (1997) 70.
- [12] C. Couprie, G. Sagon, A. Lautié, 1^{er} colloque du Programme franco-allemand de recherche pour la conservation des monuments historiques, Karlsruhe, 1993, pp. 246–249.
- [13] C. Macquet, Ph.D. thesis, France, Poitiers, 1994, 198 pp.
- [14] H.G.M. Edwards, J.F.K. Tait, *Appl. Spectrosc.* 52-5 (1998) 679.
- [15] D.C. Smith, C. Carabatos-Nedelec, M. Bouchard, *GEORAMAN'99, ABSTRACTS, Special Pub.*, Valladolid Univ. Press, Spain, 1999, pp. 36–37.
- [16] M. Bouchard-Abouchacra, Ph.D. thesis, France, Paris: Muséum National d'Histoire Naturelle, 2001, 360 pp.

- [17] M. Bouchard, D.C. Smith, "ART 2002": 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Univ. Antwerp, vol. 152, 2002, Abstract.
- [18] D.C. Smith, H.G.M. Edwards, in: A.M. Heyns (Ed.), ICORS Capetown'98, John Wiley, Chichester, 1998, p. 510.
- [19] D.C. Smith, Congress GEORAMAN-2002, Acta Universitatis Carolinae, Geologica, Praha, 46-1 (2002) 84–86.
- [20] D.C. Smith, in: M. Maggetti, B. Messiga (Eds.), Proceedings, 32nd Internat. Geol. Congress, Florence, August 2004, Spec. Pub. Geol. Soc., London, 2006, p. 9.
- [21] D.C. Smith, C. Carabatos-Nedélec, in: I. Lewis, H.G.M. Edwards (Eds.), A Handbook on Raman Spectroscopy, Marcel Dekker Inc., New York, 2001, p. 349.
- [22] L. Nasdala, D.C. Smith, R. Kaindl, M.A. Ziemann, in: EMU Notes in Mineralogy, EMU School on Spectroscopic Methods in Mineralogy, A. Beran, E. Libowitzky, (Eds.) 2004, pp. 281–343.
- [23] D.C. Smith, in: H.G.M. Edwards, J. Chalmers (Eds.), Raman Spectrometry in Archaeology and Art History, The Royal Society of Chemistry, London, 2005, p. 335.
- [24] M. Bouchard, D.C. Smith, Spec. vol., Proceedings, congress GEORAMAN-2002, Prague, 2002, Spectrochim. Acta 59A (2003) 2247–2266.
- [25] M. Bouchard, D.C. Smith, in: H.G.M. Edwards, J. Chalmers (Eds.), Raman Spectroscopy in Archaeology and Art History, The Royal Society of Chemistry, London, 2005, p. 429.
- [26] J. Lafond, Le vitrail: origine, technique, destinées, Florilège ed., France, 1992, 221 pp.
- [27] T. Furukawa, K.E. Fox, W.B. White, J. Chem. Phys. 75 (1981) 3226.
- [28] S.M. Brekhovskikh, St Gobain Glass, Stelko Keram, Aubervilliers (1982) 10–12 (documentation).
- [29] G.Y. Yu, Z.X. Shen, ICORS'2000, Wiley & Sons, Beijing, China, 2000, pp. 556–557.
- [30] J.C. Wang, Y. Yan, X.B. Zhang, ICORS'2000, Wiley & Sons, Beijing, China, 2000, pp. 588–589.
- [31] B. Schreder, W. Kiefer, in: I. Lewis, H.G.M. Edwards (Eds.), Handbook of Raman Spectroscopy, Marcel Dekker Inc., New York, 2001, p. 491.
- [32] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Spectrochim. Acta 53A (1997) 2159.
- [33] P. Colomban, Asian Chem. Lett. 5-3 (2001) 125.
- [34] R.J.H. Clark, L. Cridland, B.M. Kariuki, R. Withnall, J. Chem. Soc., Dalton Trans. (1995) 2577.
- [35] I.R. Beattie, T.R. Gilson, J. Chem. Soc. A (1970) 980.
- [36] C.A. Melendres, Electrochim. Acta 37-15 (1992) 2747.
- [37] D. Abourazzouk, Ph.D. thesis, Univ. Paris, France, 1996, 132 pp.
- [38] T. Chen, W. Weng, G. Liao, ICORS'2000, Wiley & Sons, Beijing, China, 2000, 676–677.
- [39] D.C. Smith, A. Barbet, J. Raman Spectrosc. 30 (1999) 319.
- [40] K.L. Brown, R.J.H. Clark, Anal. Chem. 74 (2002) 3658.
- [41] M. Pinet, D.C. Smith, B. Lasnier, "La Microsonde Raman en Gemmologie", Revue de Gemmologie, no. spécial hors série, AFG, Paris (1992) 11–61.
- [42] M. Pinet, D.C. Smith, Schweiz. Miner. Petrog. Mitt. (Bull. suisse) 73-1 (1993) 21.
- [43] D.C. Smith, in: Proceedings, 6th International GEORAMAN congress, Hawaii, Spectrochim. Acta, Part A, 61 (2005) 2299–2314.
- [44] W.P. Griffith, in: R.J.H. Clark, R.E. Hester (Eds.), Spectroscopy of Inorganic-Based Materials, John Wiley, New York, 1987.
- [45] H.G. Bachmann, H. Everts, MDAIK 36 (1980) 33.
- [46] B. Gratuze, I. Soulier, M. Blet, L. Vallauri, Revue d'Archéométrie 20 (1996) 77.
- [47] I. Soulier, B. Gratuze, J.N. S. Barrandon, International symposium on Archaeometry, Tubitak Ankara, 1996, p. 133.
- [48] D.L.A. De Faria, S.V. Silva, M.T.D. Oliveira, J. Raman Spectrosc. 28 (1997) 873.
- [49] D. Le Fur, Pigments et colorants, Editions CNRS, Paris, 1990, 181 pp.
- [50] P. Colomban, F. Treppoz, J. Raman Spectrosc. 32 (2001) 93.
- [51] B.O. Mysen, J.D. Frantz, Chem. Geol. 96 (1992) 321.
- [52] D.W. Matson, J. Non-Cryst. Solids 58 (1983) 323.
- [53] P.F. MacMillan, in: G. Turrell (Ed.), Raman Spectroscopy, Developments and Applications, Academic Press, London, 1996, p. 463.