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Study of XVth and XVIth century painted enamels through scientific analysis: causes of glass deterioration

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Introduction

Renaissance painted enamels are among the glass objects most precious and most affected by decay in French and foreign museums. To study their deterioration is a contribution to the study of all the old decayed glasses conserved in humid atmospheric conditions (e.g. enamels, glass vessels, flat glass). The mechanisms involved are very similar, depending on the environment. In the past decades a large number of enamels are showing signs of deterioration. White powder deposits and fractures of the glass surface produce not only a loss of transparency but also an irreversible loss of material.

The study of painted enamels is part of a research project on glass degradation which has three goals: the first aim is to identify the origin of the problem from the chemical point of view, the second is to study and understand the mechanisms and the third is to find solutions for the conservation of objects in trying to limit their decay.

Before the start of this project a major investigation in all French collections was done in the 1980s [1] showing that the decay of blue, wine coloured and purple enamels was related to a limited manufacturing period between roughly 1480 and 1530. After this period, these three colours are no longer degraded. Furthermore there is no decay manifestation for the green and brown-yellow enamels throughout the whole production period. Consequently, the cause of degradation must be a modification of glass-making recipes.

Some results have also been published giving some information on the enamelling technique and glass analysis (Michaels 1964, Smith et al 1987, Eveno et al 1990 Perez et al 1991; 1993, laboratory reports). Yet these studies were restricted either in the number of samples analysed or in the methods of examination. So, they do not give a representative view on the choice of the chemical compositions for each stable or unstable colours.

Liquid or gaseous water is the main agent causing glass degradation. Glasses will react more or less with water, depending on their chemical composition. The compositions which are easily decaying will be called unstable and those with better resistance to an aggressive environment will be called stable compositions (or unstable and stable working period, respectively).

In this paper we will present some results on the origin of the object's decay, achieved by an ion beam elementary glass analysis of a group of painted enamels dated from the XVth and XVIth c.

Choice of the art objects

Twenty painted enamels, coming from the Musée National du Moyen Age, the Musée du Louvre, the Musée du Petit Palais in Paris and the Musée National de la Renaissance in Ecouen have been investigated both technically and analytically. These enamels have been chosen from the most well documented regarding their date of production. Around half of them dates from the end of the XVth c. to the beginning of the XVIth c. – the unstable period with signs of degradation – while the other half dates from the beginning to the end of the XVIth c. – a stable period without any problems. *Le calvaire* (fig 1) is the only enamel of this group precisely dated and signed by Nardon Penicaud in 1504. The other enamels are attributed to different enamellers or schools on the basis of their style - Leonard Limosin, Jean 1st Penicaud, Colin Nouailher, Montvaerni, "le maître aux grands fronts (the master of high foreheads)", "le maître de Louis XII (the master of Louis XII)" and "le maître de l'Enéide (the master of Enéide)".

With some samples of decayed and not decayed painted enamels it was possible to study the working technique, and the properties of hydrated glass as well as to establish a systematic non-destructive analytical method of the glass surface.

Most of the art objects in this study are made by superimposing three sheets of glass on a 1 to 2 mm thick copper plaque: a first dark translucent one (often wine-coloured) from 150 to 400 μm , a second one white opaque from 30 to 50 μm and a third one coloured translucent from 300 to 400 μm (fig 2). The final layer sometimes present signs of deterioration on the surface (fig. 3). A few objects are made by a different technique - a "paillon" (thin sheet of gold or silver) superimposed on the copper plaque is covered by only one sheet of coloured glass. More information about the technique is given by Germain Bonne et al (1996).

Art objects analytical method

The glass surface has been analysed using the ion beam PIXE and PIGME method (protons induced X and gamma rays) directly on the art objects with the accelerator AGLAE from the laboratory (tandem 2MV Pelletron 6SDH-2 - NEC). A 2.8MeV protons beam is produced by a duoplasmatron source. The beam, extracted through a 8 μm kapton foil exit window, is not only able to analyse the painted enamels without sampling them but also to suppress the charge effects and to reduce the heating under the beam - which are both important for insulators. Three detectors were used simultaneously (fig 4).

The X ray spectra are recorded by two Si(Li) Kevex detectors, located at 45° (Calligaro et al 1996):

- from 0.3 to 10 keV (Na to Fe) with the small detector (10mm², resolution 140eV (5.9keV), 0.25 μm base nitrure de bore window, 0.4 μm C, helium flux),

- from 5 to 40 keV (Fe and traces elements) with the big detector (50mm², resolution 180eV (5.9keV), 6 μm Be window, 49 μm Al filter).

An Ortec HpGe detector, located at 45° in a front geometry (resolution 2keV (1.33MeV)), allowed us the determinations of sodium with the 439keV gamma rays coming from the nuclear reaction, $^{23}\text{Na}(p,p_1\gamma)^{23}\text{Na}$.

The diameter of the beam is of 1mm on the target, the beam current is 1nA and the acquisition time between 300 and 600s. The X ray spectra are evaluated with a GUPIX software (Maxwell

et al 1989) and calibration was done with reference glasses. The accuracy is about a few percents (between 5 and 10%). The given analytical data (tables 1 and 3) are average values with the sigma values of three measurements taken at different areas on the same enamel colour.

Limits of the method

Among the numerous chemical and structural modifications which occur during degradation (Libourel and al 1995, Ryan 1995, Biron and al 1999), the diffusion of water inside the glass surface produces an exchange of soluble elements, mainly the alkaline and alkaline-earth with occasional dissolution of the silicate network.

The penetration depth of a 2.8MeV proton beam in these enamels is around 75µm, but the totally analysed glass thickness depends on the elements and does not exceed around thirty micrometers. In fact, this depth is limited in PIXE mode by the X ray absorption in the glass and in PIGME mode by the cross section of the gamma ray production.

The unstable enamels have a hydrated layer of around 200µm thick, which is half of the total thickness of the coloured glass (fig 2). Consequently, the PIXE and PIGME enamel surface analysis will be an analysis of the hydrated layer only.

Stable enamels, even if they are not deteriorated, still have a hydrated layer of much less than one micrometer. Because of the weak transmission percentages for the lowest X rays of sodium, magnesium and aluminium ($I/I_0 > 60\%$ for a thickness below one micrometer), these elements will be more or less underestimated by PIXE, depending on their impoverishment in the hydrated layer. Yet this is most significant for the sodium content and less for the magnesium and aluminium compared to the intact glass (fig 5). Consequently, the intact glass sodium amounts will only be given by the PIGME measurements for which the high energy gamma ray absorption is negligible and the $^{23}\text{Na}(p,p_1\gamma)^{23}\text{Na}$ nuclear reaction yield is high up to a depth of around thirty micrometers.

If the ion beam surface analysis of stable enamels are compared with SEM - EDX (scanning electronic microscope - energy dispersive X spectrometry) cross section analysis of intact glass samples the following results were obtained:

- the sodium measurements given by PIGME correspond well with those of intact glass whereas the PIXE measurements underestimate the sodium content by around 65% (table 1),
- magnesium is the only element registered by PIXE which can in some cases be slightly underestimated compared with intact glass (not more than 10 - 15%).

Stable painted enamels - nature of the glass

Green enamels (40 analyses in total), turquoise (5 analyses) and brown-yellow ones (25 analyses) made in the XVth and XVIth c. are always stable. On the contrary the blue (30 analyses), purple (5-10 analyses) and wine-coloured enamels (5-10 analyses) are stable for a manufacturing time from the middle till the end of the XVIth c. and unstable before that period.

The glasses used for all of these enamels are alkaline silicates, mainly sodic with low contents of potassium (table 1). Our results are in correspondence with fabrication recipes of XVIth c.

Limoges enamelling reported by B. de Vigenère in 1615 [de Vigenère 1615]. The enamellers then used sand or pebbles (60-65% SiO₂) and as alkaline source the ash of marine plants (salicornia) from the sea-shores of the Provence or Spain which contained much sodium (13-15 wt.-% Na₂O). However, the content of potassium (4-6 % K₂O) is somewhat too high to be brought into the glass by the sodaash alone (Biron et al 1995). It is possible but not certain, that potassium-rich ashes of fern or wood (beech, oak...) were used together with salicornia.

The white opaque glass is special in that it contains crystals of tin oxide in a matrix of lead-silicate (table 2).

The colouring elements are cobalt associated with iron for the blue elements (the recipes of B. de Vigenère mention the addition of "l'ajout de saphre", cobalt oxide), copper for turquoise colours ("cuivre brûlé et saphre") and copper together with iron for the green ones ("cuivre brûlé par cinq jours en lames tenues", copper in thin sheets calcinated for five days), iron with manganese for brown-yellow ("rouille de fer", rust of iron), copper, iron and manganese for purple ("saphre") as well as tin and lead for opaque white ("deux parties de plomb pour une d'étain de Cornouaille", two parts of lead with one part of tin from Cornwall).

The manganese source was "pierigot", a black stone from the surroundings of the city Périgueux.

The comparison of trace elements with the colouring elements shows that in the green enamels copper is correlated with zinc (0.06 wt.-% ZnO), both coming from brass and that iron is associated with cobalt. For the brown-yellow enamels with high levels of manganese this colouring element is associated with iron and strontium (0.03 %). Finally, the cobalt sources of the blue enamels also contained iron, manganese, nickel, rubidium, arsenic and bismuth (figs. 6a and 6b) – the sources are similar but not identical to those exploited in Germany in XVth to XVIIIth c. Europe (Gratuze et al 1992).

The production of stable painted enamels follows the same tradition in the choice of ingredients of the glass batch – nature and proportion of silica and alkaline sources are the same, the same colouring elements were used as well but in other proportions. Therefore numerous characteristics are observed in the analysed objects regarding the content of metals (see o values in table 1). This shows that the recipes for glass fabrication were not strictly fixed but allowed certain individual freedom. The following two examples demonstrate these particularities: some of the brown-yellow enamels contain less than 1.5 % Mn whereas the others contain between 1.5 and 5 %. Furthermore some objects are totally or partly enamelled with lead-rich glass having 10 to 20 % PbO whereas the others contained less than 1 %. These characteristics do not seem to be connected to a specific enameller or a particular workshop. The principal component analysis shows two groups for the blue enamels (not depending on the degradation), two for the brown-yellow and one for the green enamels. This statistic evaluation of the given data will be published soon.

The unstable painted enamels – glass nature and cause of corrosion

The blue enamels (in the sum 30 analyses), the wine-coloured (5-10 analyses) and purple ones (5-10 analyses) made between the end of the XVth and the beginning of the XVIth c. are always chemically unstable. The same colours become stable in the second half of the XVIth c. The ion beam analyses correspond to those made at the surface of hydrated glasses. To identify the differences in chemical composition between the stable and unstable enamels of these three colours, it is necessary to distinguish between compositional modifications caused by alteration

and those caused by different manufacturing recipes. Generally, in the hydrated layer an important loss of sodium and potassium is observed, to a lesser degree there is a decrease of magnesium and aluminium with occasional enrichment of sulphur (fig. 5).

Among the differences between stable and unstable enamels which can not be induced by alteration are the higher concentration of potassium and copper in the degraded enamels of the three colours whereas lead occurs in increased content in the stable blue enamels (tables 1 and 3). Clearly these differences can be attributed to a modification of glass recipes. Lead and copper contents are not significantly affected during hydration, whereas potassium is one of the most soluble elements (fig. 5). The latter therefore must have had a higher initial content of about 6-8 % K_2O in the unstable enamels compared to only 4-6 % in the stable ones. This was confirmed by electron probe microanalysis of intact glass made on a cross-section of an altered enamel sample. This analysis of the first layer of intact purple glass (on the copper plaque) gave 10 to 13 % K_2O and Na_2O , respectively (table 2).

In conclusion it can be stated that the enamellers have used a sodium source of vegetable origin for the unstable enamels as well, but added higher amounts of potassium-rich materials in comparison to the stable glasses.

The ratio of the average concentrations of potassium and aluminium in unstable enamels is two times higher than in that of stable enamels of blue, wine-coloured and purple colour ($K/Al_{\text{unstable}} = 2x K/Al_{\text{stable}}$). On the other hand the same ratio of average contents of copper and aluminium varies for different colours – it is three times for blue enamels ($Cu/Al_{\text{unstable}} = 3x Cu/Al_{\text{stable}}$), 40 times for the wine-coloured and 12 times higher for purple. These results suggest potassium sources of a different nature for the stable and unstable enamels. The strong enrichment of copper in the latter glasses could be derived from salpêtre or niter (mainly potassium nitrate) the fabrication of which a recipe by Agricola (1556) describes as being a mixture of "rich soil", chalk, ash of oak (or wood) and water. The recovered and recycled water was heated to boiling and then decanted several times. After that the concentrated solution was poured into a tub containing copper bars on which the salpêtre crystallised. It is probable that the different contents of copper observed according to the colours prove different procedures with varying crystallisation times. Furthermore, the input of salpêtre or tartar was recommended by the XVIth c. Limoges enamellers for giving the glass "the colour and brightness of pearls" (de Vigenère 1615). Indeed the unaltered enamels of wine-colour and purple (the blue in less extent) have a darker and duller tint compared with those in brown-yellow and green. It therefore seems likely that the enamellers wished to bring out lighter and more brilliant colours at the beginning of the production at the end of the XVth and beginning of the XVIth c.

The glassmakers probably noticed after about 50 years of production that the blue, wine-coloured and purple glasses which were rich in potassium (13-15 % Na_2O and 10-13 % K_2O) were starting to deteriorate. Since the second quarter of the XVIth c. they therefore made all of the coloured enamels according to the recipes of the green and brown-yellow enamels which were stable silicates less rich in potassium (13-15 % Na_2O and probably 4-6 % K_2O).

The introduced colouring elements and opacifiers (for white glass) are the same for stable and unstable enamels. Nevertheless a major part of unstable enamels used cobalt sources different to the other glasses – cobalt is always correlated to iron, manganese, nickel and rubidium but most of the unstable enamels contain significantly lower amounts of arsenic and bismuth (see figs. 6a and 6b).

Relation structure - chemical stability

The unstable enamels contain more modifying elements such as potassium and copper than the stable enamels. This fact contributes to the depolymerisation of the structure and so they become more easily affected by the environment. The higher the number of broken bindings T-O-T or non-bridging oxygens (T: metallic cation Si, Al... and O: oxygen atom) divided by the total number of tetrahedrons (NBO/T) [2] the more the glass structure is depolymerised. For the unstable blue, wine and purple enamels, the average NBO/T values [3] are indeed somewhat higher than those of the same stable colours.

- blue stable enamels: NBO/T = 0.89 - unstable = 0.93,
- purple stable enamels NBO/T = 0.79 - unstable = 0.90,
- wine stable enamels NBO/T = 0.97 - unstable = 0.99.

Nevertheless, if these results seem to confirm the close relation between the hydration capacity and the depolymerised character of a glass, already shown for glass windows (Sterpenich 1998), this non-bridging structural parameter cannot be the only one to explain the different chemical stability observed. All individual NBO/T stable enamel values (between 0.55 and 1.20) for all colours are little lower than those of unstable enamels (between 0.7 and 2.0), but still these two groups overlap one another. So these results prove that for the same depolymerised state, the nature and ratio of the chemical elements are playing a basic role in the glass stability, in promoting more or less the dissolution and the different movable species in the hydrated layer [4].

Conclusion

For all the painted enamels investigated in this study dating from the XVth c. to the XVIth c. Limoges enamellers have used high sodium silicate glass batches with plant ash sodium sources - compositions which are typical for the South of France and Mediterranean countries as early as since the Middle Ages. The choice of sodium sources, colorants and opacifiers (white glass) are generally those described in the XVIth c. recipes. Nevertheless, if the object's analyses present many particularities, they are not related to specific enamellers or schools. This proves a kind of freedom in the working process.

The degradation observed has been seen to depend on the chemical composition of the enamels. The decayed blue, wine and purple enamels which date from the XVth c. to the beginning of the XVIth c. contain more potassium and copper than the stable enamels. The addition of potassium and copper probably comes from saltpetre, which was recommended to produce a more brilliant glass. From the beginning to the end of the XVIth c. the blue, wine and purple enamels become stable as the other colours, which are always chemically stable whatever the working period.

As follows from the average compositions the unstable enamels have a more depolymerised structure than the stable ones which makes them more vulnerable to a humid environment. After all, this tendency is not always verified if we consider the individual analyses. So, the nature and ratio of the chemical elements appears to be very important to reinforce or damage the glass chemical stability.

Acknowledgements

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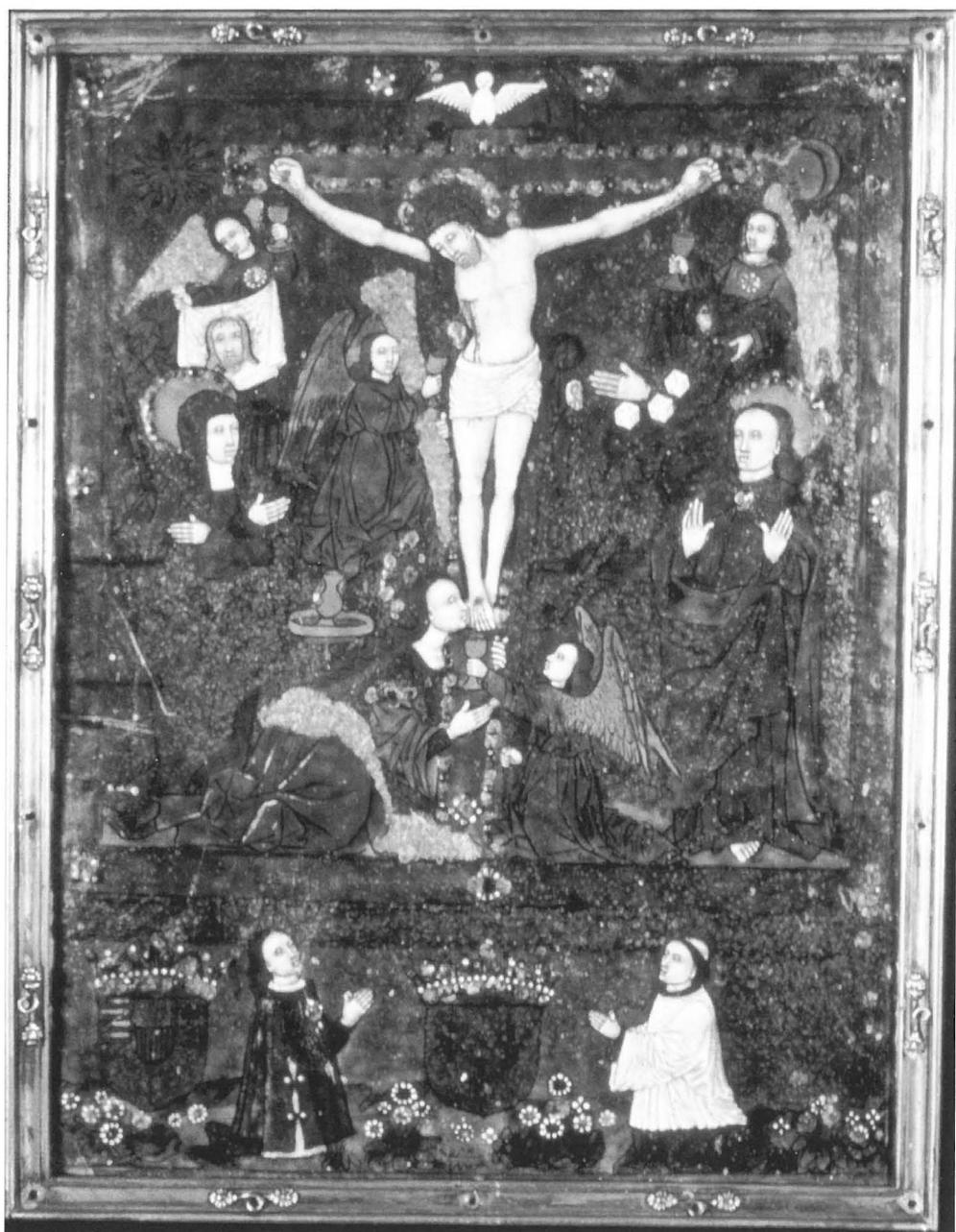


Fig. 1: Le Calvaire - Musée national du Moyen Age et des Thermes de Cluny (N°inv Cl 15154)

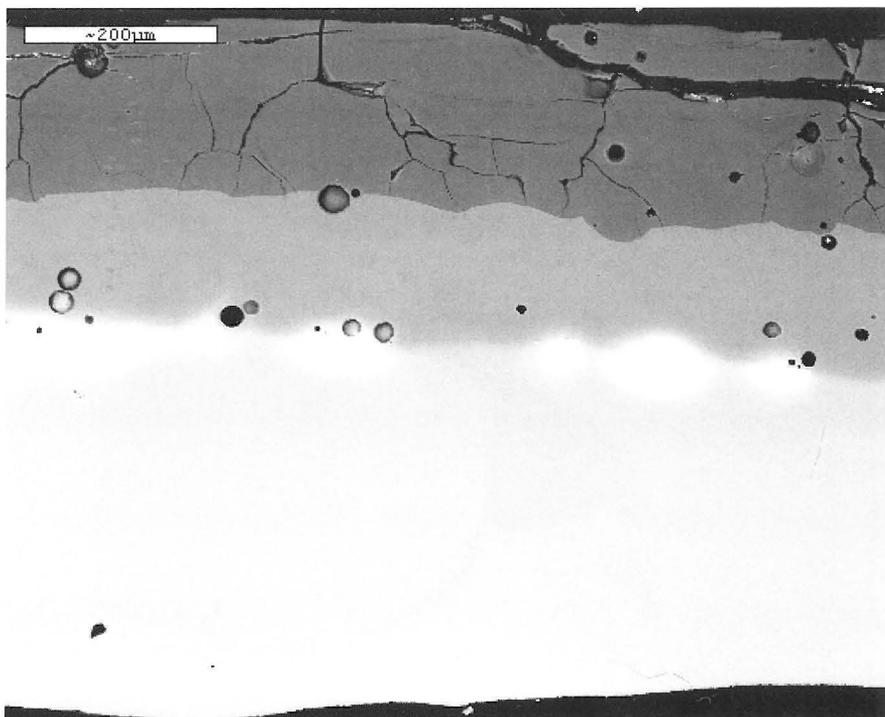


Fig. 2: Backscattered electron image of a decayed blue XVth c. painted enamel cross section: below a first dark layer of glass on the copper, in the middle a white opaque layer of glass, on the top a blue degraded sheet (in dark grey colour 200 μ m of hydrated fractured glass and in pale grey intact glass).

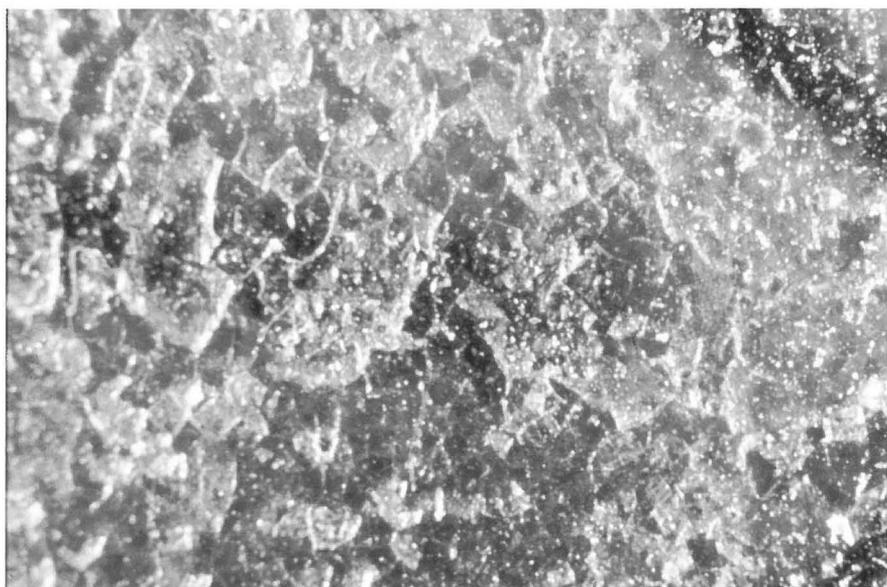


Fig. 3: Detail of the deteriorated glass surface of a blue XVth c. enamel (crizzling)

wt-%	Na ₂ Ox	Na ₂ O _γ	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	CoO	CuO	SnO ₂	PbO
blue	5.17	14.49	2.17	1.38	63.31	0.34	0.62	0.83	3.90	4.68	0.68	1.42	0.34	0.75	0.27	3.12
	σ	1.48	0.57	0.38	6.55	0.23	0.83	0.30	0.85	0.93	0.64	1.02	0.18	0.70	0.48	7.19
purple	5.49	15.37	2.32	1.41	66.13	0.24	0.20	0.84	4.09	4.70	1.84	1.09	0.15	0.04	0.04	0.75
	σ	2.42	0.28	0.18	0.07	0.18	0.23	0.25	0.33	0.45	0.12	0.47	0.01	0.03	0.02	1.03
wine	5.20	15.18	2.49	1.55	61.95	0.48	0.52	0.82	6.43	5.10	3.43	1.22	0.06	0.02	0.04	0.13
	σ	2.43	1.21	0.37	3.62	0.49	0.63	0.29	3.13	0.84	1.86	0.79	0.10	0.01	0.04	0.12
yellow-brown	6.72	12.48	1.20	1.20	57.69	0.13	0.70	0.54	5.87	4.43	2.80	10.52	0.02	0.15	0.10	1.46
	σ	4.73	0.49	0.40	8.64	0.22	0.86	0.27	2.19	1.63	1.80	5.20	0.11	0.20	0.11	4.42
green	5.58	12.74	1.19	1.24	62.08	0.11	1.02	0.61	5.02	3.70	0.53	5.92	0.08	3.94	0.18	1.28
	σ	3.45	0.52	0.54	7.20	0.16	0.83	0.21	1.73	1.39	0.93	3.46	0.12	1.93	0.23	4.00
turquo	6.56	14.77	1.83	1.30	61.24	0.16	0.30	0.95	4.65	5.43	0.44	0.91	0.09	6.34	0.35	0.26
	σ	1.65	0.31	0.32	2.16	0.16	0.35	0.30	1.00	1.08	0.38	0.27	0.08	2.55	0.20	0.37

Table 1: Average and sigma values of ion beam chemical analysis for all stable enamels in each colour (element oxides in wt-%) / Na₂Ox and g = PIXE and PIGE measurements

wt-%	Na ₂ Ox	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	CuO	SnO ₂	Sb ₂ O ₃	PbO
dark purple	11.84	1.64	3.13	54.87	0.85	0.25	0.71	13.40	8.38	5.71	0.48	0.13		0.61	
white	9.17	0.14	0.15	42.66	0.05	0.89	1.15	6.54	1.02	0.22	0.3	0.26	13.05		19.7

Table 2: Average values gained by energy-dispersive X-ray spectrometry (scanning electronic microscopy) chemical analysis (in wt-%) obtained on the cross section of a XVth c. sample: the first layer of purple glass and the second of white opaque (stable glasses)

wt-%	Na ₂ Ox	Na ₂ O _γ	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	CoO	CuO	SnO ₂	PbO
blue	3.42	4.12	1.15	1.03	66.80		1.60	0.47	5.20	3.90	0.49	2.12	0.57	1.28	0.16	0.78
	σ	2.66	0.46	0.20	5.49		0.80	0.24	2.37	1.63	0.40	1.58	0.46	1.08	0.18	2.56
purple	5.81	5.06	1.52	1.28	74.61	0.28	1.45	0.49	5.60	5.00	2.26	1.00	0.18	0.43	0.08	0.41
	σ	3.14	0.21	0.16	5.14	0.21	0.63	0.21	1.55	0.90	1.78	0.26	0.02	0.20	0.03	0.51
wine	2.70	2.42	1.58	1.12	72.99		0.94	0.55	8.05	5.53	4.65	0.64	0.04	0.61	0.05	0.45
	σ	1.92	0.15	0.08	9.90		0.18	0.33	4.79	2.72	3.96	0.37	0.05	0.77	0.05	0.45

Table 3: Average and sigma values of ion beam chemical analysis for all unstable enamels in each colour (element oxides in wt-%) / Na₂Ox and g = PIXE and PIGE measurements

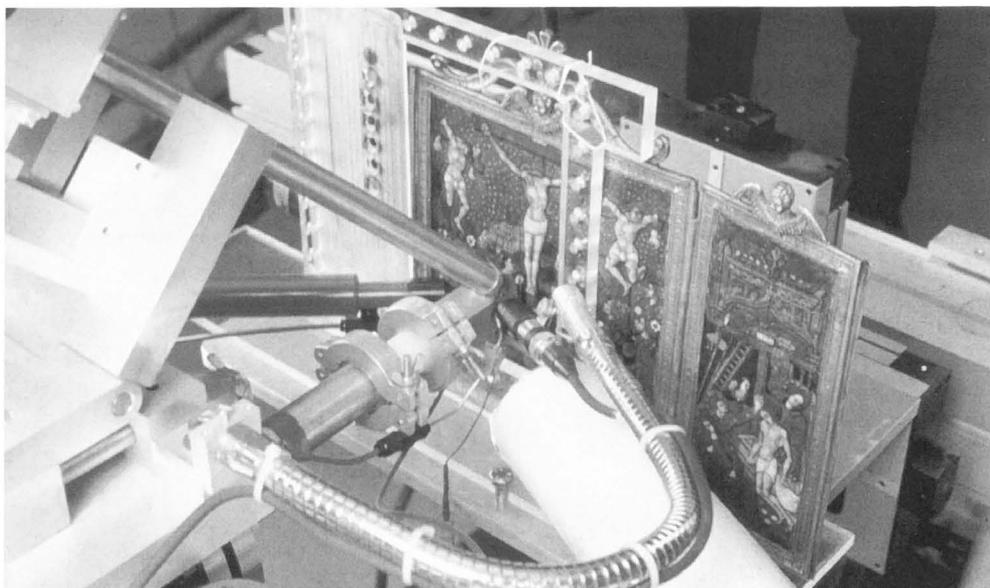


Fig. 4: Overview of the AGLAE accelerator analytical external beam set up - triptyque de la crucifixion du Musée du Louvre (N° inv OA947) ready for analysis - three detectors and helium flux

depth profiles

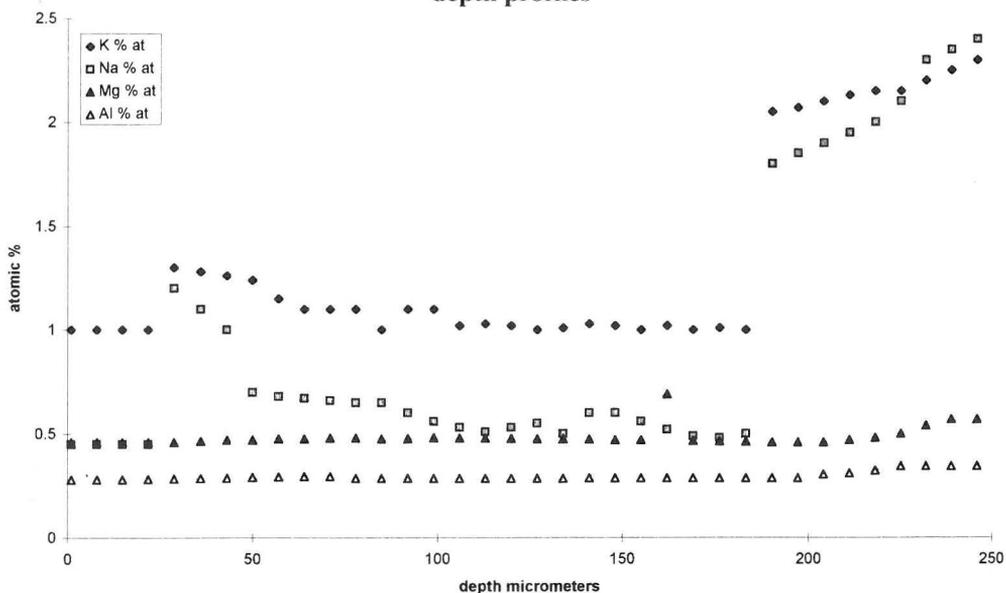
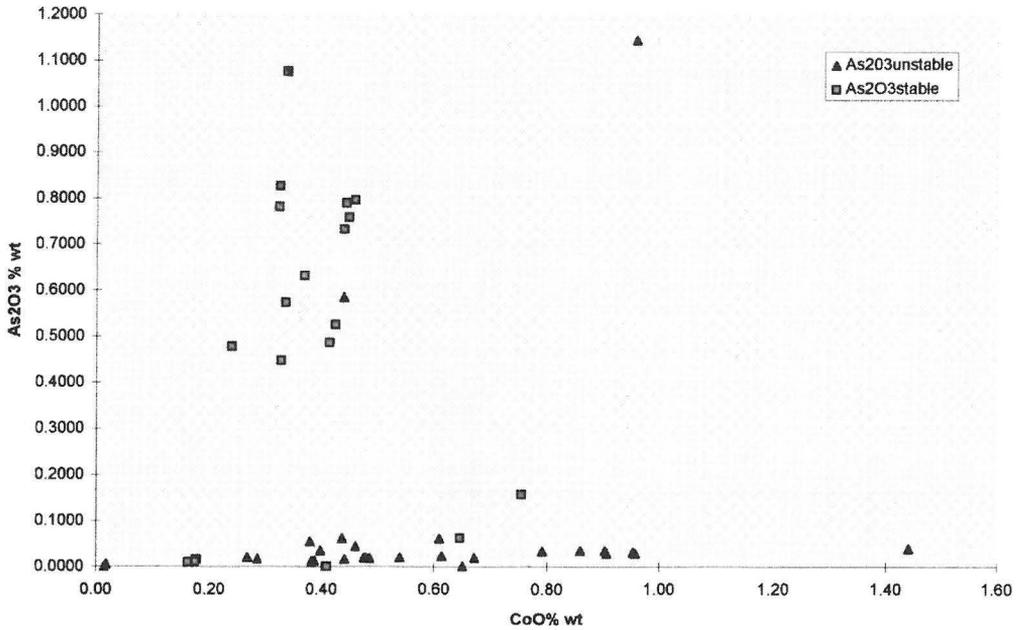


Fig. 5: Depth concentration profiles for sodium, potassium, magnesium and aluminium in atomic % obtained by electron probe microanalysis (wavelength-dispersive X-ray detection) from the surface (depth 0 μ m) into the intact glass (above 190 μ m - at 27 μ m; fracture) - blue XVth c. painted enamel

Blue stable and unstable enamels



Blue stable and unstable enamels

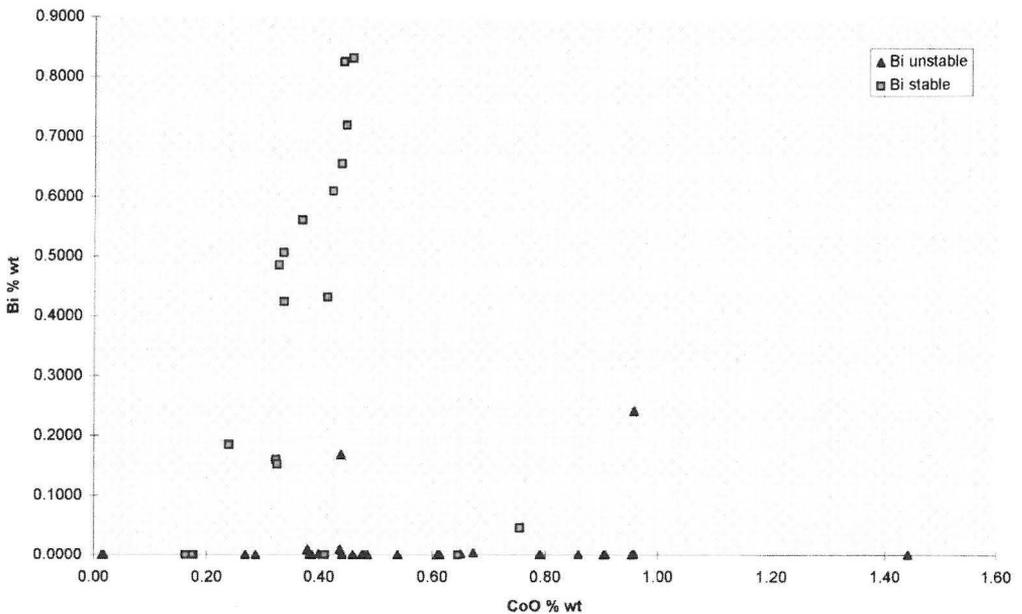


Fig. 6a and b: Cobalt contents versus arsenic (a) and bismuth contents (b) for all blue stable and unstable painted enamels (PIXE measurements)

Notes

1. Co-ordinated by the Services de Restauration de Versailles in collaboration with the Laboratoire de Recherche des Musées de France.
2. Formulas used are different depending of the authors, here : $NBO/T = 1/T(\sum_{i=1}^n nM_i^{n+})$
 - T number of cations in tetrahedral sites
 - M number of cations (i) modifying elements (deduced from the number of charge compensators)
 - n charge of the cation i.
3. Calculations including the intact glass sodium values for the unstable glasses, around 15% Na₂O (EDX measures on samples)
4. Dominique Germain Bonne dissertation, will be finished at the end of 1999.

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