

Preparation and properties of model glasses of historic enamels of the Green Vault Museum, Dresden

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Many enamelled art objects of the Green Vault Museum, Dresden, have been suffering a severe deterioration of the enamel layers during the last 20 to 30 years. The authors obtained three splinters of about 200 mg weight each of green, blue, and opaque turquoise enamel of the Aurangzeb ensemble. Model glasses of these originals were prepared which should match them as closely as possible. The investigations showed that the simple degree of network polymerization related to the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio is insufficient to understand their chemical properties even if one takes components such as MgO , CaO or Al_2O_3 also into consideration. To understand further structural influences IR, UV/VIS, and EPR spectroscopy studies were performed on the enamels, and it could be evidenced that components such as MnO , Fe_2O_3 , CuO , CoO , PbO and SnO_2 not only act as colorants or opacifiers but also as stabilizers of these materials. Taking this into account the chemical and physical behavior of the respective enamels in the museum can be elucidated.

1. Introduction

In the first third of the 18th century, August II (1670 to 1733), also called Augustus the Strong, reigned as Elector over Saxony and as King over Poland. In his residence in Dresden he inaugurated one of the most famous baroque art collections, the Green Vault. Today this museum contains about 3000 art objects, e. g. precious stones, golden and rock crystal goblets, ivory and especially many extremely valuable enamelled pieces. Perhaps the most important figures ensemble is that of the “Court to Delhi on the Birthday of the Great Mogul Aurangzeb”, consisting of 132 pieces. Many of the partly golden figures are decorated by one or more layers of painting enamels, which mask the golden substrates. Others are enamelled by translucent layers of green, blue, red and yellowish colors, respectively, which are shiny to the chased golden background. Most of them are also set with diamonds [1].

Over the past 20 to 30 years a severe deterioration of the enamel layers of the historic art objects has been observed, consisting of crizzling, loss of adhesion and even peeling off, accompanied by a more or less strong chemical corrosion of the glassy coatings. In a first investigation these damages were described carefully. It could be shown that the cause of these degradation processes – besides others – can be seen in the increased evolution of environmental pollutants, e. g. SO_2 and NO_x from combustion processes, and sub-

stances like acetic acid and formaldehyde from the wood, textiles, adhesives and lacquers of the display cases, also in interaction with a water vapor containing atmosphere [2]. In the project “Model Conservation Concept for Precious Enamel Objects Damaged by Pollution in the Green Vault”, running from 1997 to 1999, three major topics were tackled:

- finding an explanation for this type of damage,
- eliminating or reducing the danger, and
- stabilizing the enamels by attaching the loose enamel layers.

A summary of the most important results and conclusions of this study was published by the project partners in 11 articles in [3].

The objective of our contribution to this project consisted in studying the adhesion process of the historic enamels on the noble metal alloys, including a description of the specific adhesion mechanisms [4 and 5]. Since work with the original objects was not possible, model glass substances of some of the historic enamels had to be prepared. This paper describes preparation and some properties of these model glasses matching as closely as possible a blue enamel, susceptible to corrosion and to crizzling, a green enamel, peeling off layer by layer from the substrates, and a relatively stable opaque turquoise enamel.

2. Experimental

At the beginning of our work the Green Vault Museum delivered the three original enamel splinters shown in figure

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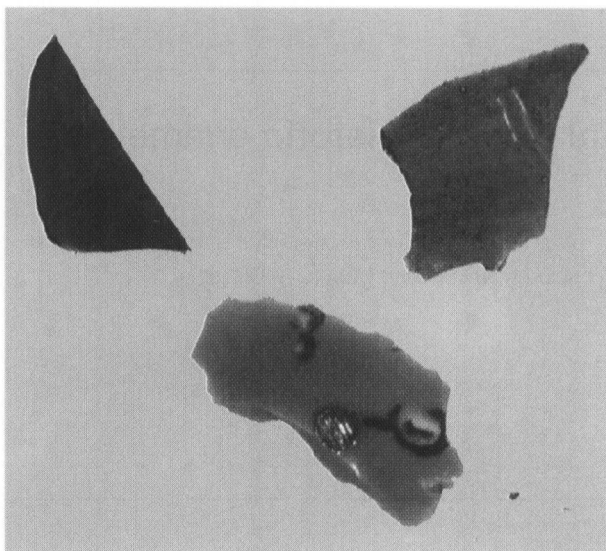


Figure 1. Photograph of the original enamel splinters from the Aurangzeb ensemble of the Green Vault Museum, Dresden.

Table 1. Chemical composition in mol% of the original enamels

component	green	blue	turquoise
Na ₂ O	19.03	21.39	19.22
MgO	0.65	0.00	0.00
Al ₂ O ₃	1.09	0.68	0.29
SiO ₂	65.06	70.25	59.60
SO ₃	0.57	0.72	0.00
Cl ⁻	0.65	0.97	0.00
K ₂ O	1.95	1.86	2.09
CaO	3.07	0.75	1.44
MnO	0.25	0.00	0.00
Fe ₂ O ₃	1.55	0.30	0.00
Co ₂ O ₃	0.00	0.36	0.00
CuO	6.13	2.72	2.56
SnO ₂	0.00	0.00	8.85
PbO	0.00	0.00	5.94

1, which had to be returned undestroyed and unchanged at the end of the work. These enamel splinters of about 200 mg weight each are from the Aurangzeb ensemble. Table 1 contains the compositions of these three enamels, obtained by X-ray fluorescence analysis (XFA) [2]. All three of them are alkali oxide-rich glasses (>20 mol%). The green enamel is ionically colored by Mn, Fe, and Cu, the blue one by Fe, Co, and Cu, whereas the turquoise enamel is a PbO-containing material opacified by SnO₂. The raw materials (oxides and carbonates) were mixed well, the PbO-free batches were melted for 1 h at 1350 °C in a Pt(Au) crucible in a laboratory furnace in normal air, for melting the PbO-containing batch an Al₂O₃ crucible was used with a melting at 1400 °C also in normal air. The melts were poured on a steel plate at room temperature and after cooling the glasses were ground and sieved to a fraction with a grain size between 63 and 140 μm. The enamelling on the noble metal alloys was performed by firing at 850 °C for 4.5 min with an average thickness of the enamel layers of ≈ 400 μm [6].

The densities of the model enamels were determined by the pycnometer method, using water as a liquid. These densities were used then to calculate the molar volumes. The

infrared (IR) spectra were obtained with a double beam spectrometer of the type PU 9712, Philips, Kassel (Germany). The KBr technique was used with 3 mg of the enamel (grain size < 63 μm) embedded in 3 g KBr. The transmission in the ultraviolet/visible part of the optical spectrum (UV/VIS) was measured by an OMEGA-10 double beam spectrophotometer, Bruins Instruments, Puchheim (Germany). 25 μm thick slices of the model enamels, glued to a microscope slide glass, were investigated in transmission, in comparison to a microscope slide glass and the glue as a standard. Additionally, the color action of the chromophores was assessed in comparison to a RAL color fan [7] with the glasses enamelled on a noble metal alloy substrate of Au75/Cu15/Ag10 composition. Further the colors were determined as color coordinates L, a, b according to the international CIE-Lab system [8]. The investigation of the paramagnetic centers produced by the transition metal ions was performed by an electron spin resonance (EPR) spectrometer of type ER 200 D-SCR, Bruker Analytische Meßtechnik GmbH, Rheinstätten (Germany). Samples of 30 mg in silica glass tubes were applied and the measurements were done at room temperature. This instrument was available at the Institut für Angewandte Physik, Technische Universität Clausthal.

3. Results and discussion

Taking only the simple molar SiO₂/Na₂O ratios of the three compositions according to table 1 into account, the blue enamel should be the most stable substance. However, neither the damages found in the museum nor a laboratory test confirmed this. This test of the hydrolytic stability of model glasses according to DIN ISO 719 displayed an unexpectedly good performance of the green enamel, a relatively good behavior of the turquoise enamel and a by far worst stability of the blue enamel [2]. This discrepancy between the high stability of the green and the low stability of the blue enamels can be understood with the help of Newton's schematic ternary diagram of historic glasses [9], see figure 2. In the middle of this diagram there are the relatively stable glass compositions A, M, R, whereas the glasses H, J, K at the right hand side are less stable. The glasses W, Z at the left hand side are decomposing already in the museum atmosphere. The three enamel compositions according to table 1 are denoted in figure 2 by the small letters b (= blue), g (= green) and t (= turquoise). Whereas the composition g lies beyond the chemical stability borderline with an R^{HO} content of ≈ 10 mol% in the field near the stable glasses A, M, R, the composition b is in the range of the unstable glasses W, Z, see also [10]. From this diagram it is clearly seen that not only the SiO₂ content determines the chemical stability of these glasses but also the R^{HO}, the "R¹₂O" and the "SiO₂" contents. The green enamel has an R^{HO} (CaO, CuO, and MgO) content of 9.85 mol%, in contrast to the blue enamel with 3.47 mol% only. Due to its two positive charges Cu²⁺ acts as a stabilizer in the network and the same is true for the intermediate ions Al³⁺ and Fe³⁺, which may substitute Si⁴⁺ and trap the charge compensating alkali metal ions. A part of the SnO₂ of composition t is dissolved as the stabilizing network former Sn⁴⁺ in the glass network, whereas the remaining SnO₂ is acting as an opacifier as small crystals. An influence of the packing density of the glass network on the chemical stability does

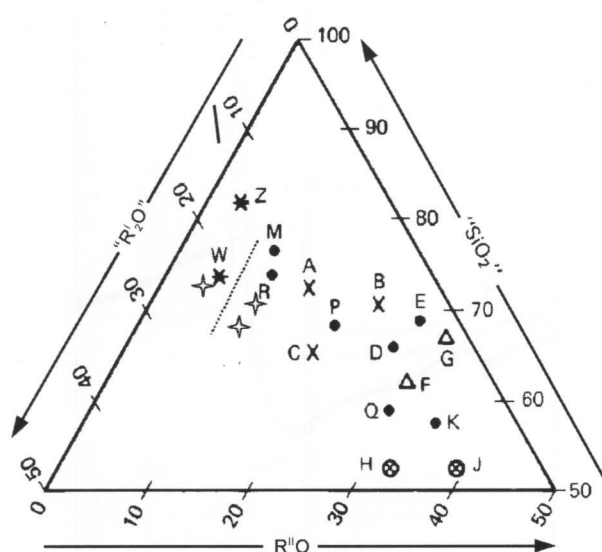


Figure 2. Modified Newton's diagram [9] of ternary compositions of historic glasses (capital letters) and investigated enamels (small letters) of the Green Vault; " $R^I O$ " = $R^I_2O - (Al_2O_3 + Fe_2O_3)$, " SiO_2 " = $SiO_2 + Al_2O_3 + Fe_2O_3 + SnO_2$, $R^{II}O$ = CaO, MgO, MnO, CuO .

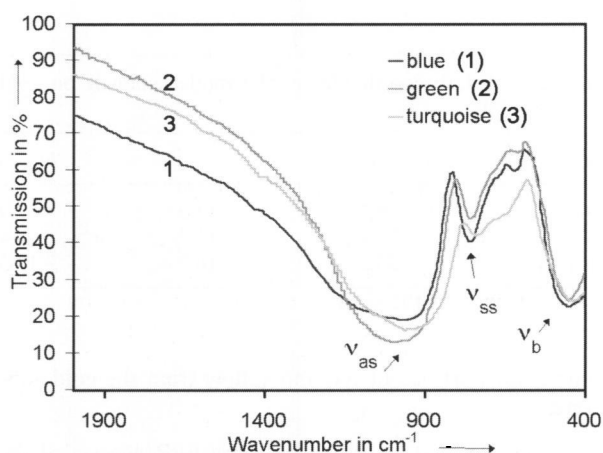


Figure 3. IR spectra of the model enamels.

not seem to be present, since the molar volumes of all three enamels lie near 14.1 cm^3 , despite the differing density values of $(2.671 \pm 0.005) \text{ g/cm}^3$ (green), $(2.55 \pm 0.01) \text{ g/cm}^3$ (blue), and $(3.317 \pm 0.008) \text{ g/cm}^3$ (turquoise). Pb^{2+} ions should widen the glass structure [11], however, this is not reflected by the molar volume of composition t, possibly due to the contracting action of the dissolved Sn^{4+} ions, but mainly also because the SnO_2 crystals diminish the molar volume due to their own molar volume of 11.1 cm^3 and the high density of 6.89 g/cm^3 [12]. Obviously the actions of the Pb^{2+} ions and the SnO_2 crystals compensate for each other in the turquoise enamel.

The IR spectra shown in figure 3 possibly allow conclusions with respect to the degree of network polymerization of the model enamels, see the positions of the asymmetric valence vibration ν_{as} , the symmetric valence vibration ν_{ss} , and the bending vibration ν_b of the $-Si-O-Si-$ groups. Vibration ν_{as} of the blue enamel shows a band near 960 cm^{-1} apart from the vibration near 1100 cm^{-1} . Both

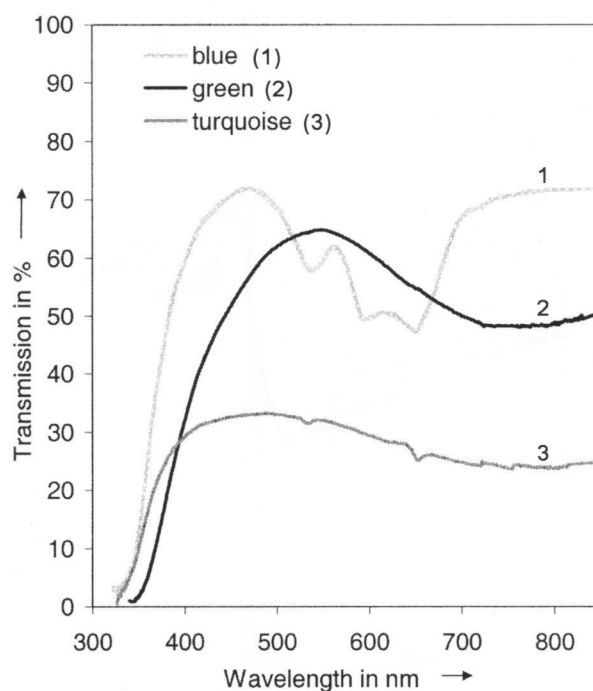


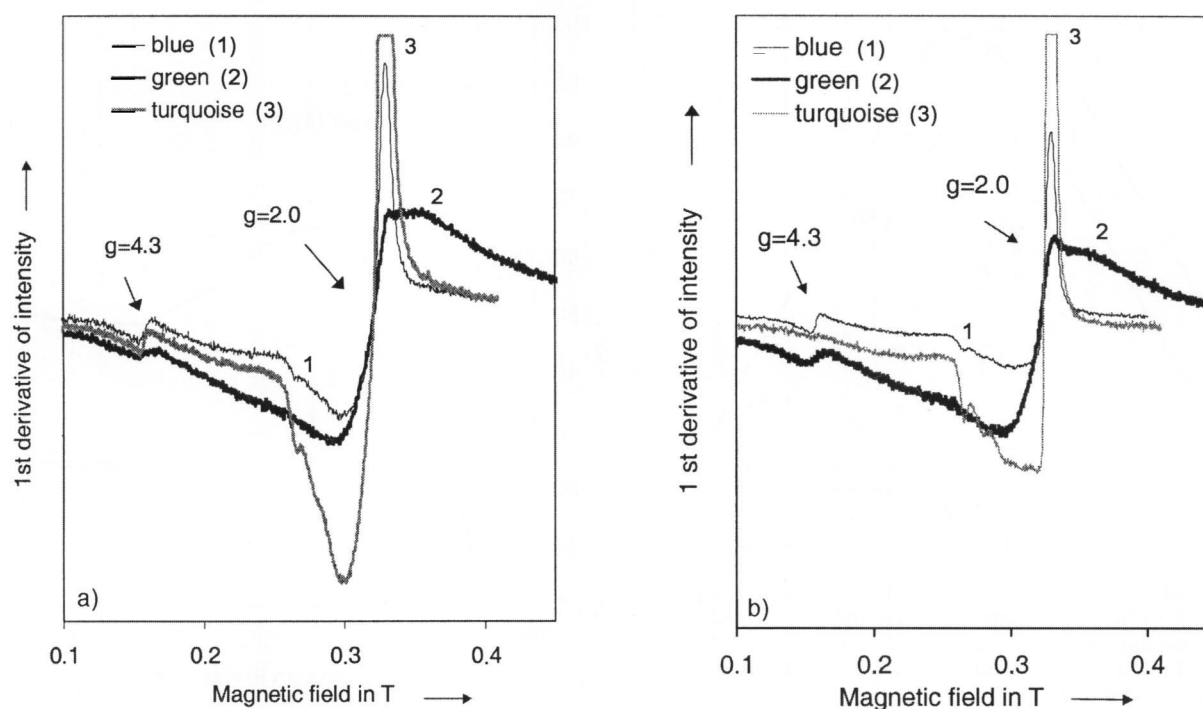
Figure 4. UV/VIS spectra of the model enamels.

the green and the turquoise enamels also display strong absorptions at 960 cm^{-1} , with a shift towards $\approx 940 \text{ cm}^{-1}$ for composition t. In the case of binary alkali metal silicate glasses the shift of ν_{as} from 1100 to 960 cm^{-1} is caused by network modifying groups such as $-Si-O-Na^+$. However, if ions with di- or trivalent valences are also present in the glass, such a band shift may also occur [13]. Intermediate oxides may form heterogeneous chains with SiO_4 tetrahedra, thus impeding realistic conclusions on the degree of polymerization.

The blue and the green enamels show ν_{ss} minima at 750 cm^{-1} , the turquoise enamel at 740 cm^{-1} . According to Neuroth [14] the intensity decreases with increasing alkali oxide content, in accordance with the finding that with decreasing SiO_2 content in the order blue, green and turquoise enamels the band intensity decreases. Although the blue enamel has a higher alkali metal oxide content than the green one, due to its higher SiO_2 content the band is more pronounced than that of the green enamel. Moreover, the content of divalent ions lowers the intensity and causes a shift to higher wavelengths, as observed for the influence of PbO [14]. This may also explain the lower intensity of ν_{ss} of the turquoise enamel.

The bending vibration ν_b is observed at 450 cm^{-1} for the blue and the green enamels and at 430 cm^{-1} for the turquoise enamel. Also in this case PbO influences the band position with a shift to higher wavelengths and a reduction of the intensity.

According to Bukovec and Kosec [15] and Carturan et al. [16] the shoulder at 660 cm^{-1} of the turquoise enamel may be attributed to SnO_2 vibrations. Sn^{2+} is an ion with high field strength, thus compacting the glass structure in the dissolved state and opacifying it above its solubility border as SnO_2 crystals. The network former Sn^{4+} strongly improves the chemical stability of the PbO containing enamel and shifts the band to lower wavenumbers.



Figures 5a and b. EPR spectra of a) original enamels, b) model enamels at 293 K.

In contrast to the IR spectroscopy UV/VIS and EPR spectroscopies are capable also of monitoring both the valency and the coordination of transition elements. Because of their dependence on the redox state, investigations are necessary for a correct assessment. Figure 4 displays the UV/VIS spectra of the model enamels. Compared to $\text{Na}_2\text{O}-\text{SiO}_2$ glasses the position of the UV cut-off of the model enamels is shifted to longer wavelengths. Thus the cut-offs of the blue and turquoise enamels are situated at 350 nm, that of the green enamel at 370 nm. Partially such a shift is caused by a high concentration of network modifiers. However, the green enamel shows the strongest shift, although its alkali metal oxide content is lower than that of the blue enamel. The reason for this may be seen in the high content of transition elements, since both tetrahedrally and octahedrally coordinated Fe^{3+} ions are responsible for the band between 365 and 375 nm [17]. A comparison with the RAL color fan delivers a moss-green color (RAL 6005), a combination between yellowish green [Fe^{3+}O_4] and yellowish brown [Fe^{3+}O_6] [18]. Possibly also a band at 420 nm, caused by [Mn^{2+}O_6], may influence the color [19].

The blue coloring Cu^{2+} ions lead to a distinct band at ≈ 780 to 790 nm, in coincidence with a finding of Prescott of an absorption at 798 nm for octahedrally coordinated Cu^{2+} in tetragonal distortion [20]. The turquoise enamel also has a strongly broadened band near 780 nm, slightly shifted to shorter wavelengths, in accordance with [19]. Due to the scattering SnO_2 crystals the transmission of the turquoise enamel is low.

The blue enamel shows a triple band between about 500 and 600 nm, which originates from the strongly coloring [Co^{2+}O_4] complex. Its extinction coefficient is high, giving a low color lightness coefficient L and a value of RAL 5002 (ultramarine blue). For the turquoise enamel one obtains RAL 5018 (turquoise blue). All spectroscopic color values are gathered in table 2. The translucent enamels also contain

Table 2. CIE-Lab coordinates of the model enamels on gold substrates [8]

enamel	L	a	b
blue	26.5	17.6	-32.9
green	33.1	-11.3	4.4
turquoise	53.2	-18.2	-10.3

some color portions of red and yellow from the gold substrate.

Figures 5a and b display both the EPR spectra of the original enamel splinters and of the model enamels. The spectra of all original enamels show a clear resonance with a Landé factor of $g = 4.3$, which normally is attributed to the network forming [Fe^{3+}O_4] group [21]. A comparison of the EPR spectra of the enamels in figures 5a and b shows that they are very similar, except for the Fe_2O_3 content in the case of the turquoise original enamel. This is due to an art decoration by a painting enamel, see the dark dots on the corresponding splinter surface in figure 1.

The turquoise original contains Cu^{2+} ions with characteristic lines around $g_{\parallel} = 2.3$ and $g_{\perp} = 2.08$, showing a hyperfine structure (hfs) with four lines through the isotopes ^{63}Cu and ^{65}Cu with a nuclear spin of $I = 3/2$ [21]. According to Bogomolova et al. [22] this points to a cubic center with tetragonal distortion. Poole et al. [21] measured $g_{\parallel} = 2.371$ and a coupling constant $A_{\parallel} = 151$ G, which is in good agreement with the present data. The agreement of $g_{\perp} = 2.025$ and $A_{\perp} = 24$ G is less good with the present results. Due to the small coupling constant this hyperfine structure is badly resolved only. Likewise the existence of [Fe^{3+}O_6] with a g value of 2 cannot be unambiguously evidenced due to the line superposition with the g_{\perp} value of the [Cu^{2+}O_6]

complex. Possibly the $[\text{Fe}^{3+}\text{O}_6]$ broadens the line width of the Cu^{2+} center at $g = 2$.

The blue original has an Fe resonance of $[\text{Fe}^{3+}\text{O}_4]$ at $g = 4.3$, which might be overlapped by a Co resonance of $[\text{Co}^{2+}\text{O}_4]$ normally detectable at 4 K only [23]. Cu^{2+} and Fe^{3+} resonances are also to be seen at $g = 2$. Noticeable is the weak development of the Cu^{2+} hfs. For higher concentrations of the centers the EPR signals appear distorted and their characteristic features disappear. Moreover, an exchange interaction between neighboring Cu^{2+} centers may also cause the disappearance of the hfs. This both holds for the original and the model enamels.

The green enamel shows a $g = 4.36$ resonance of the network forming Fe^{3+} . A superposition of a Cu^{2+} hfs is not detectable, possibly because of the strong exchange interaction due to the high CuO content of 6.13 mol%. Moreover, Fe^{3+} and Mn^{2+} superimpose the $g \perp$ signal of Cu^{2+} , leading to a broadening of the resonances at low g values. After Prescott [20] the Fe^{3+} spectrum contains a peak at $g \approx 9$ and a broad signal with low intensity at $g \approx 2$. High contents of Fe^{3+} lead to a broadening of the 4.28 signal and of the resonance at $g \approx 2$ [20]. Nofz et al. [24] interpret the broad resonance at $g \approx 2$ as a spin-spin exchange interaction of the Fe^{3+} ions.

Other explanations interpret the $g \approx 2$ resonance as an effect of Fe^{3+} ions with an antiferromagnetic coupling, as the presence of antiferromagnetic $\text{Fe}^{3+}\text{-Fe}^{2+}$ clusters and ferromagnetic phases like Fe_3O_4 , respectively. This signal is only detectable at Fe_2O_3 concentrations of 0.1 to 5 mol%, as is the case for the green enamel. Prescott [20] also found three differing Fe^{3+} signals at $g = 8.1, 4.28$ and 2. The latter signal was partially superimposed by the Cu resonance. These three signals point to differing surroundings of Fe^{3+} in the glass, moreover, an influence of Cu^{2+} on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox ratio seems to be evident. With increasing CuO content the intensity of the $g = 2$ signal of the Fe^{3+} increases and that of the 4.3 signal decreases.

UV/VIS and EPR spectroscopies point to the presence of the following structural units: $[\text{Cu}^{2+}\text{O}_6]$, $[\text{Fe}^{3+}\text{O}_4]$, $[\text{Fe}^{3+}\text{O}_6]$, and $[\text{Co}^{2+}\text{O}_4]$. Although these groups, especially $[\text{Cu}^{2+}\text{O}_6]$, partially have network modifying character, in total because of their relatively high field strength compared to alkali ions they stabilize the -Si-O-Si- glass network [11 and 21]. The total amount of the oxides MgO, Al_2O_3 , MnO, Fe_2O_3 , CoO, and CuO, being in the position to act as intermediate oxide stabilizers, is 9.67 mol% for the green enamel, compared to 4.06 mol% for the blue one. Despite its lower SiO_2 content and its lower SiO_2 -based degree of network polymerization, the green enamel is more stable than the blue one. This is mainly due to the Cu^{2+} and the Fe^{3+} ions. The transition metal ions thus do not only act as coloring agents but also as stabilizers in these two enamels. This also explains the position of these enamels in Newton's diagram, see figure 2. In the case of the turquoise enamel both stabilizing Pb^{2+} and the network forming Sn^{4+} ions determine its relatively good chemical stability.

In conclusion, these investigations show that the model enamels match the originals very well, which means that the studies on adhesion processes and mechanisms as well as physical properties obtained on the model enamels [4 to 6] may be transferred to the original art enamels.

4. Conclusions

The Green Vault Museum in Dresden possesses about 3000 art objects, among which are many extremely valuable enamelled pieces, e. g. the Aurangzeb ensemble. During the past 20 to 30 years a severe deterioration of the enamel layers has been observed. We obtained three splinters of about 200 mg weight each of a green, a blue, and an opaque turquoise enamel and prepared model glasses which should match these materials as closely as possible. The glasses were melted from the raw materials in normal air. It turned out that the molar ratios $\text{SiO}_2/\text{Na}_2\text{O}$, i.e. the degree of network polymerization, of the three compositions is not sufficient to understand their chemical stability. One has to take into account also the other components present in the materials. Thus the green enamel contains besides MgO, CaO, Al_2O_3 also components like MnO, Fe_2O_3 and CuO as colorants, the blue enamel contains also CoO, whereas the turquoise enamel has high amounts of PbO and SnO_2 . To elucidate the structural influences of these different components, IR, UV/VIS, and EPR studies were performed. It could be shown that complexes like $[\text{Cu}^{2+}\text{O}_6]$, $[\text{Fe}^{3+}\text{O}_4]$, $[\text{Fe}^{3+}\text{O}_6]$, and $[\text{Co}^{2+}\text{O}_4]$ are present in the materials and that these components – dependent on their abundance – may also stabilize the structures. Moreover, Pb^{2+} can stabilize the glasses, too, as does Sn^{4+} , which acts as a network former below its solubility limit. Precipitating SnO_2 crystals opacity the turquoise enamel.

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