

Influence of environment on the corrosion of glass–metal connections

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Abstract ‘Glass sensors’ of the eighteenth century Backer glass and the sixteenth century enamel from Limoges have been chosen for a series of experiments. Combinations of these materials with different base materials such as copper and bronze has been investigated. To create surface changes on the ‘glass sensor’, a corrosion process was induced in a controlled environment. A variety of corrosive agents such as hydrochloric acid, sulfuric acid, water and formaldehyde were used. The sample immersed in the corrosive solution was exposed alternately to light and high temperature for a total of 38 weeks. During this period, macroscopic and microscopic observations were made and series of tests such as SEM/EDS and Raman spectroscopy were performed on the surface of the samples. ICP-MS methods were used to determine the change in the chemical composition of the solutions where the samples had corroded. The primary aim of this study was to identify the impact of a number of external corrosive variables such as temperature, humidity and local environment to identify the most damaging environments for glass–metal objects. The obtained results showed the chemical and physical phenomena acting on the surface of

the glass, metal or in the place of their joints. Information obtained on this study was used to explain the influence of the environment on the surface of glass–metal materials. Results can be used in the design of conservation work as well as for sustainable conservation.

1 Introduction

Historical objects represent material proof of human activity and are the testimony of a bygone era. Each artifact brings not only historical value, but also carries artistic and scientific merit. Therefore, they require special care and personal attention to maintain their condition. Corrosive agents appear on the material’s surface and over time objects can be destroyed [1]. Physical and chemical changes due to mechanic deterioration as well as chemical reactions between glass elements and its surrounding environment cause deterioration of the objects [2, 3]. There are many examples of objects where glass and metal are connected for both esthetics and functionality. A significant group of historical glass–metal objects used in this research were enamels from Limoges and the eighteenth century Backer glass.

The painted enamels, produced during the Renaissance period in Limoges, are unique and extraordinary due to their figurative composition and creative achievements. Their uniqueness is also apparent given the technological knowledge about melting and the expansion properties of the glass flux that the workshops had [4, 5]. The enamels can show signs of deterioration, induced through the chemical composition of the enamels, humidity, temperature and atmospheric pollution [6]. These implications cause an irreversible loss of the material’s mass and changes in color and the transparency of the glass [7]. The

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Renaissance brought, especially to the royal court, not only richly decorated enamels, paintings and furniture but also glass crockery and cups which were often fitted with metal parts. The mechanism of corrosion of glass objects from that period is well known. In previous studies, glass diseases such as crizzling, crazing, weathering and glass crystallization are documented [8–10]. Also, the corrosion of metal objects was frequently described in the literature [11, 12]. Corrosion of stained glass and enamel has been described, largely focusing on the corrosion of individual components [13]. However, what is still missing is information on the mechanism of corrosion of glass-to-metal objects and the impact the environment has on the crystallizing on the surface products.

There are many corrosion catalysts, depending on the material causing the deterioration of the surface. Metals can be the subject of two kinds of corrosion: chemical or electrochemical (galvanic). Glass corrosion is primarily the result of hydrolysis, leaching, weathering and progressive crystallization—which is a natural occurrence through the passage of time [14]. Finally, corrosion of objects containing both metal and glass is caused by reactions occurring first on the weakest material-metal and later on in the connecting areas of metal to glass. Identifying reactions on the surface of historical object is a subject that interests many researchers. However, using original materials is irrational as during the test a lot of materials may be destroyed.

The biggest limitation and challenge are the amount of samples. In previous studies, non-destructive methods in historical research are described [15, 16]. However, they are still unable to say with absolute certainty that the analysis which uses light rays, radiation, laser and electron excitation does not cause any damage, especially in the future. Therefore, some pre-prepared replica glass had to be manufactured. The so-called “glass-sensor method” allowed one to produce an unlimited amount of material for experiments of induced corrosion processes as well as other tests without damaging any historical—perhaps valuable—original pieces [17].

The aim of this study was to determine the most aggressive environment for a group of glass-metal historical objects. ‘Glass sensors’, which were the subject of a series of aggressive process, were used for this study. Corrosion changes on the surface of the material were diagnosed and the mechanisms of corrosion of glass-to-metal objects were determined. Results can be used in the design of conservation work as well as for sustainable conservation—providing optimal storage conditions for glass-metal objects.

2 Materials and methods

The glass sensor used in this research was created based on the chemical composition of an eighteenth century glass

Table 1 Composition (wt%) of compounds used to prepare the blue enamel, the Limoges enamel reproduction

Compound	Beaker glass	Enamel	Compound	Beaker glass	Enamel
SiO ₂	73.94	43.26	Fe ₂ O ₃	0.06	0.13
Al ₂ O ₃	0.07		CoO		0.24
CaO	9.26	1.90	MbO ₂		0.39
MgO	0.59		CuO		1.36
BaO	0.14	0.75	ZnO		0.06
K ₂ O	14.28	9.73	B ₂ O ₃	0.65	
Na ₂ O	0.84	16.68	TiO		0.1
PbO	0.07	25.46	NiO		0.04
MnO	0.1				

beaker (Table 1). This sensor has the same chemical composition as an original antique glass with comparable chemical and physical properties, as well as similar reactive qualities. Glass with a high alkali content (Na₂O + K₂O = 15.22 %wt.), with the addition of lead oxide is technically soft and called technological long glass. Shapes are easily made during an extended period when the glass has a viscosity suitable for molding by hand.

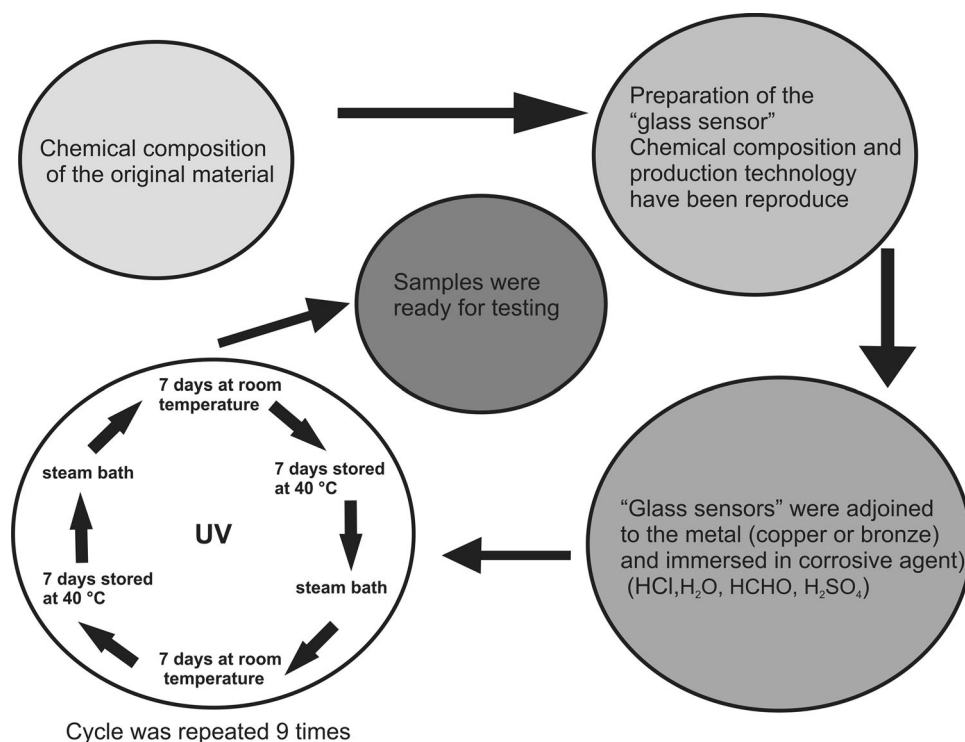
To prepare samples of enamel on copperplate, a known oxide composition of the original enamel from Limoges was used (Table 1). The blue enamel was put on the copper plate and then thermally treated. The prepared enamel has a high content of lead oxide and a low content of silica. Such glass is characterized by a high refractive index and a high density. Furthermore, the typical composition of the oxide mass of the blue coloring has been applied, with the coexistence of copper oxide (CuO), cobalt oxide (CoO), and nickel oxide (NiO).

Samples of the eighteenth century glass sensors were adjoined to pieces of metal. The next step was to place the samples consisting of glass joined with metal into various corrosion catalytic environments:

- Sample A: glass sensor + copper band, immersed in a 0.1 M hydrochloric acid HCl;
- Sample B: glass sensor + copper band, immersed in water;
- Sample C: glass sensor + brass band, immersed in water;
- Sample D: glass sensor + copper band, immersed in 0.01 M hydrochloric acid HCl;
- Sample E: enamel placed on the copper in the form of two drops, immersed in 20 % formaldehyde (HCHO);
- Sample F: glass sensor + brass band, immersed in a 0.5 M solution of sulfuric acid (VI) (H₂SO₄).

The reconstituted material as an example of glass-metal objects was subjected to corrosion induced over a period of

Fig. 1 Graphical scheme of the corrosion-induced processes



38 weeks. To accelerate the corrosion of the sample, the solutions were periodically subjected to an elevated temperature and strong light. Initially, the sample was boiled in a steam bath (4 times per hour) and in successive stages and the solutions stored at room temperature. Every other week, after 168 h, they were kept at 40 °C (Fig. 1).

To identify the most corroded points, a stereoscopic observation was made using Leica Wild M8 stereoscope. After the initial diagnosis of the areas affected by corrosion, observations were made using a microscope metallographic MET 3. Examination by SEM/EDS was performed with a scanning electron microscope, Carl Zeiss AG-EVO 40 Series. This helped to identify the quality and quantity of elements produced during experimentation on the glass and metal surface, as well as obtaining the chemical composition of both elements. The intention was also to observe the crystallized surface morphology and corrosion products on the surfaces of objects [18]. After 38 weeks of this induced corrosion, the sample's corrosion was specified through atomic emission spectroscopy—identifying the composition of the samples (ICP-MS DRCII by Perkin-Elmer). For samples B, D, E and F, further analysis of the phase composition was performed using Raman spectroscopy (Leica Renishaw DMLM). This apparatus uses two lasers at 514 and 785 nm. A single beam spectrometer was used, with a camera connected to the confocal microscope and the imaging filter set to dispersive Raman imaging.

3 Results and discussion

3.1 Stereoscope

The preliminary diagnosis indicated several significant points on the samples which were later investigated in more depth (Fig. 2). In the case samples A it can be noted that the grinding surface of the glass is much more corroded than the broken surface. Glass of a given composition (eighteenth century original glass) is presented as a glass with numerous blisters. These blisters can indeed accelerate the corrosion process. To observe the changes in sample B, a metal band was removed. The precipitate was clearly visible between the metal and the glass in the form of a brown product. Observations also indicated a considerably large amount of fogging in the glass. On sample C, a white crystallized product appeared on the surface of both the glass and metal. These places were subject to further in-depth studies. Sample D was of significant interest when subjected to corrosion. The copper band around the glass dissolved in 0.1 M HCl, and the resulting reaction formed a green crystalline corrosion on the entire surface of the glass and metal. Also, the acid solution discolored and the reaction of the chloride ion with copper resulted in the precipitation of the product being crystallized over the entire surface of the beaker. Sample E proved most complicated as the prior literature on the problem of corrosion glass–metal objects in formaldehyde is in short supply. It should be noted that

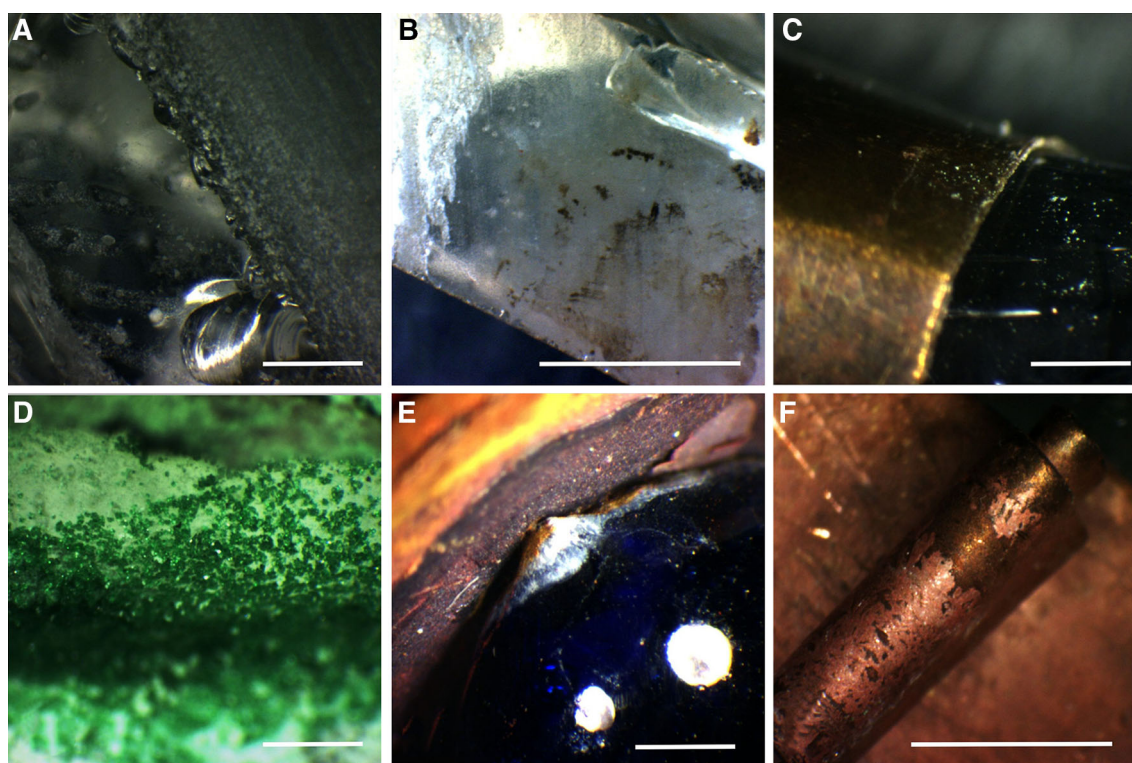


Fig. 2 Microphotographs of the samples A–F after administering induced corrosion of the samples in aqueous solutions. **a** 0.1 M HCl, **b** H₂O, **c** H₂O, **d** 0.01 M HCl, **e** 20 % HCHO, **f** 0.5 M H₂SO₄. Wild Leica M8 Stereoscope. Scalebar 20 μ m

sample E consisted of two materials which exist together. Their corrosion process must take into account some synergetic reactions. Their analysis was very complicated because of many chain reactions which are hard to distinguish from each other in the organic media. Such a sample must almost certainly be multiplied and tested separately after a defined period of time. Moreover, a change in color can be seen on the metal surrounding the glass. Corrosion products on both materials have been easily observed as a result of the build-up of material between the enamel and the metal, caused partly by the detachment of enamel from the base. In the case of sample B (glass sensor immersed in a solution of sulfuric acid), the corrosion of the glass was not evident during stereoscopic observation. Attention was attracted by the corrosion of the metal band (Fig. 2). There were clearly visible areas of corrosion and color change in the metal band, presumably the result of the oxidation reaction.

3.2 Metallographic microscope

Microscopic observations were carried out on the surface of cross-sectional layers of specially prepared samples of enamel on copperplate sample (Fig. 3). Observations showed an increase of 20 μ m, enabling the initial diagnosis of the resulting layers of corrosion. This proved an efficient

and effective way to provide information on the thickness, color and structure of the observed layers [19]. Photos from a metallographic microscope allowed for further planning and the subsequent use of SEM/EDS and RS—mitigating the need for analysis of the entire sample's surface. Photographs show the extensive changes arising from the combination of metal to glass. Red corrosion products between the materials are vividly shown by their penetration into the structure of the enamel. The red color indicates that the corrosion product is a copper oxide (I)—Cu₂O—product of oxidation of copper. The corrosion layer is thicker closer to the glass part (enamel) (Fig. 3 a, b). This suggests that the mechanisms of the corrosion accelerate in places where the ions from the solution react with components leaching from the glass. Thickness of the corrosion layer is as much as 400 μ m. Photographs taken suggest possible oxidation reactions (metal to oxide), drawing attention to the growing area of corrosion and the buildup of crystallites between the copper and enamel. As a result of this, one of the two drops of enamel lost its adhesion to the substrate and disconnected.

3.3 Scanning electron microscope

Due to the high concentration of the hydrochloric acid (0.1 M), the metal element (copper) in the sample A was

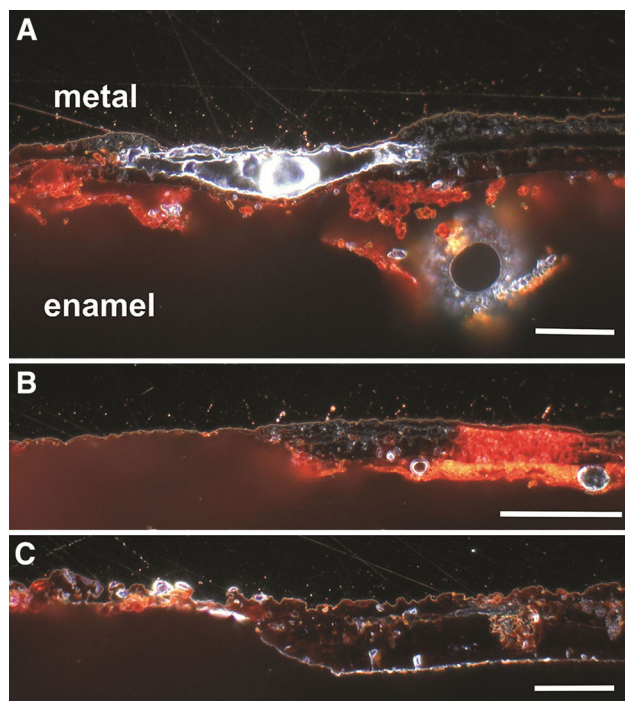


Fig. 3 Metallographic microphotographs of sample E (enamel on copperplate, the corrosion induced by 20 % formaldehyde solution). Pitting corrosion and blistering in enamel are visible. **a** Corrosion of enamel–copperplate connection. **b** Changes of corrosion layer thickness depending on the distance from the enamel. **c** The differences in the thickness of corrosion buildups. Scalebar 250 μm

completely dissolved. Therefore, further studies were based on the analysis of sample D (a lower concentration of 0.01 M HCl). Only the acid solution (0.1 M HCl from sample A), for which the metal band had dissolved, has been tested by ICP-MS (next paragraph). In the case of sample B, the metal surface in contact with the glass shows the corrosion products crystallized in the form of tetrahedrons (Fig. 4). The semi-quantitative chemical analyses by EDS on spots displayed the largest amount of copper and oxygen (oxidation products) (Table 2). What was also an interesting find, was the presence of chlorine and sulfur, most likely originating from the surrounding area.

On sample C, corrosive spherical-shaped lesions were observed (Fig. 4). The analysis made apparent the precipitate formed is a compound of copper (Cu), oxygen (O), zinc (Zn), and sodium (Na) (Table 2). Relatively high concentrations of sodium (Na) may be the result of hydrolysis and hydration, which eventually lead to the leaching of alkali from the glass.

For sample D, 13 measurements in total were made. Most of the analysis showed that the corrosion product is a compound of copper (Cu), oxygen (O) and chlorine (Cl). Also noted was the presence of carbon (C) at a concentration of <7 % by weight. It is very difficult to describe the shape of the crystallites (Table 2).

Sample E consisted of blue enamel applied to a substrate made of brass, kept in a 20 % solution of formaldehyde HCHO (Fig. 5). At the beginning, corrosion of the metal substrate away from the application site of enamel was analyzed. Then, the qualitative composition of the products of corrosion occurring around the enamel drop was determined (corrosion of metal close to enamel).

The obtained results indicated a difference in the composition of the enamel–metal corrosion layer (Fig. 5), as well as other corroded areas. The three elements in highest concentration were carbon (C: 7.8 %wt.), oxygen (O: 11.2 % by wt.) and copper (Cu: 85.1 % by wt.) (Table 2). The chlorine (Cl: 0.5 % by wt.) arises from the surrounding area before preparation and being immersed in a 20 % solution of formaldehyde. The closer to the enamel, the more prevalent elements originating from the glass were carbon (C: 6.5 % by wt.), oxygen (O: 10.11 % by wt.) and copper (Cu: 82.26 % by wt.), and also detected: Silicon (Si: 0.3 wt%) and lead (Pb: 0.8 % by wt.). Finally, an analysis was conducted on the surface of the enamel (%wt.): C-8,5; O-34,9; Al-0,2; Si-16,3; Cl-0,3; K-0,7; Ca-0,7; Cu-6,6; Pb-12,0. It could be assumed that the relatively high concentration of copper is the result of corrosion phenomena occurring at the border of enamel-to-metal, and is derived from the glass as one of the coloring oxides.

For sample F, a number of analytical tests were performed. Corrosive changes in the glass (strongly attached to the metal), and metal (without glass coating) were relatively minor. Corrosion is clearly visible on the surface of metal touching the glass—evident in the crystallized products displayed (Fig. 4). EDS analyses exhibited silicon, aluminum and potassium, all cations derived from the composition of the enamel (Table 2).

3.4 Inductively coupled plasma mass spectrometry (ICP-MS)

The results confirm the intensity of the corrosion occurring on the samples in different solutions. Table 3 indicates that the samples stored in water were moderately active ion exchanges. Metallic elements were derived from metal bands attached to the glass. The presence of copper (Cu = 14 mg/L) was observed in the solution of sample B (glass sensor + copper band). The presence of zinc (Zn = 11.5 mg/L) was noted in the solution of sample C (glass sensor + brass band). Furthermore, in samples B and C potassium was detected (respectively, 6.4 and 5.5 mg/L), this indicates that the processes of aqueous hydration, hydrolysis and ion exchange in glass have occurred. An acidic environment is yet more aggressive—causing many more chemical reactions. Either in solution A, D and F, attention was paid to the high concentration of calcium (respectively, $\text{Ca}_{(A)} = 24.7$, $\text{Ca}_{(D)} = 47.1$, $\text{Ca}_{(F)} = 15.1$ (mg/L)). It can, therefore, be claimed that the

Fig. 4 SEM image of corrosion products formed between glass and metal for samples B, C, D, F. **a** Sample B, corrosion in water; **b** Sample C, corrosion in water; **c** Sample D, corrosion in 0.01 M HCl; **d** Sample F, corrosion in 0.5 M H₂SO₄

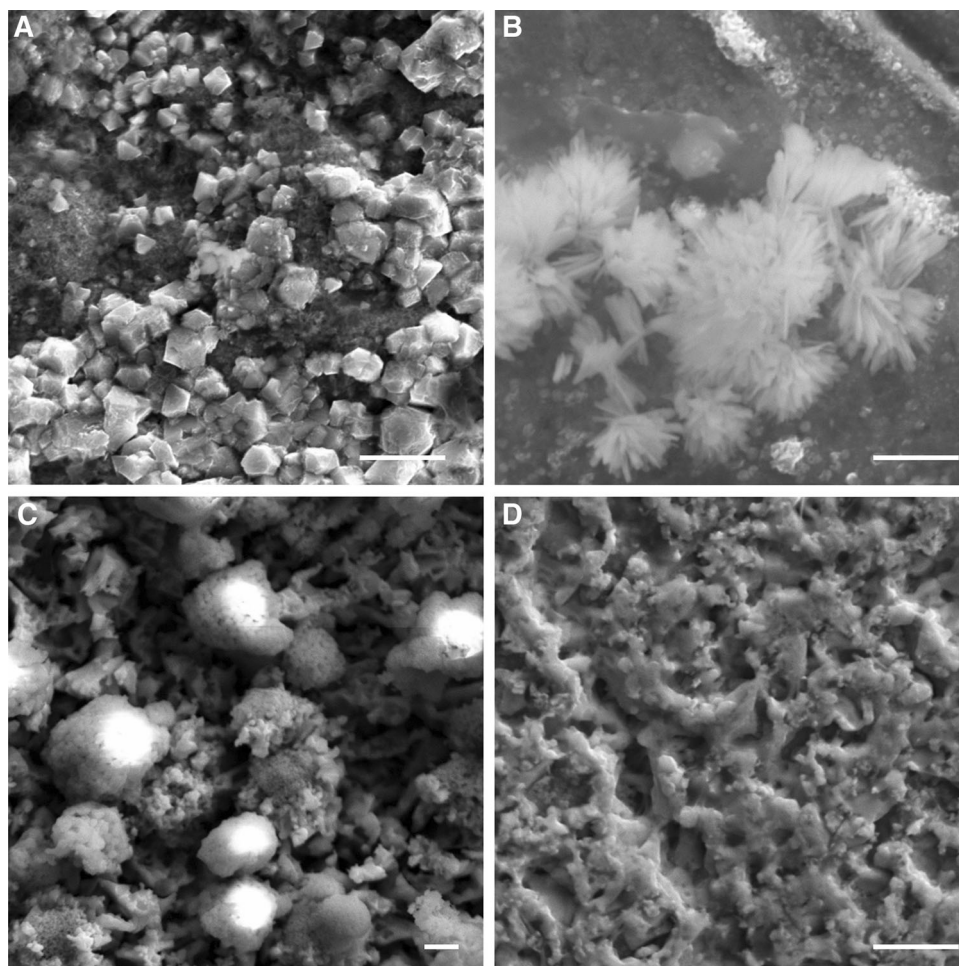


Table 2 Elemental composition of samples (SEM-EDS). Carl Zeiss AG-EVO 40 Series

Element (wt%)	Sample										
	B Glass side	B Metal	C Glass side	C Metal	D Powder	E Glass (center)	E Glass (rim)	E Glass-metal border	F Glass side	F Metal	
Cu	83.20	82.81	18.47	72.58	59.83	46.98	6.63	32.15	77.67	97.35	
Zn			31.56	5.74					1.00		
Pb						7.52	12.25	4.07			
O	5.89	15.28	26.33	13.66	21.98	13.09	34.93	32.47	6.55		
C			20.09		4.43	1.64	8.53	4.03	9.27	2.72	
Cl	0.56	1.98			19.51	0.42	0.32				
S	0.37		6.51								
Si			0.59			9.92	16.33	22.96	2.97		
Al							0.21	0.24	1.36	0.35	
Ca						0.25	0.74	0.31			
K							0.71		0.65		

exchange of alkalis are cations from glass with ions from the solution. This is confirmed by the measurable concentration of sodium and potassium. Structure-building elements of glass are detected in solution at high concentrations. This

demonstrates the glass-metal corrosion in acidic solutions. Metal ties are also dissolved at low pH levels. High concentrations of all the elements (from the vitreous-enamel material as well as metal base) in 20 % formaldehyde solution were

Fig. 5 Sample E: cross-section of researched areas (enamel applied to the base metal) and SEM/EDS analysis of enamel application site- corrosion layer.

a Visible various areas of corrosion, *scalebar* 1 mm,
b The boundary between enamel and copperplate, *scalebar* 50 μm . Carl Zeiss AG-EVO 40

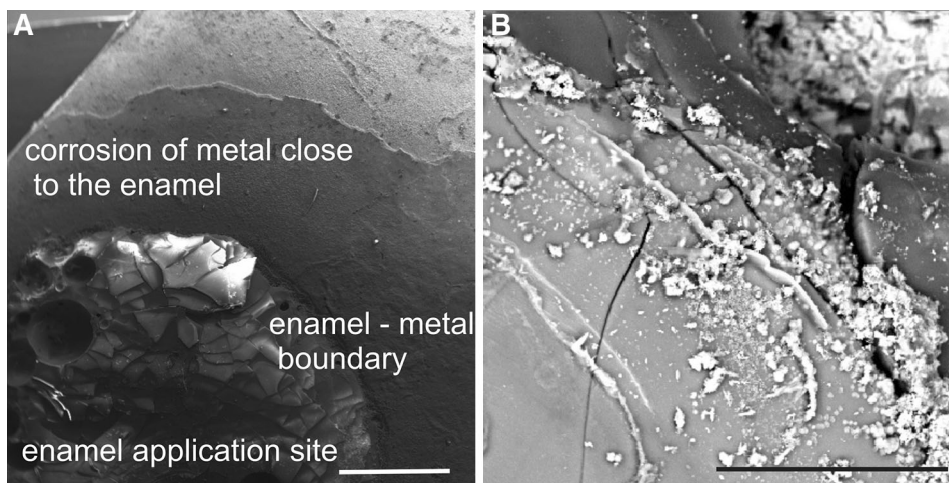


Table 3 Elemental composition of solutions after experiments

Element	Concentration (mg/L)					
	A	B	C	D	E	F
Ca	24.7			47.1	30.3	15.1
Cu	1,330	14		6,400	28	
K	7.0	6.4	5.5	8.0	8.1	5.7
Na	6.4			8.4	9.1	15.7
Zn			11.5	12.6	11.4	1,650

A 0.01 M HCl, B H₂O, C H₂O, D 0.01 M HCl, E 20 % HCHO, F 0.5 M H₂SO₄. ELAN ICP-MS DRCII by Perkin-Elmer

registered. This details the intensity of the corrosion processes in the enamel–metal object in an organic solvent. In addition to the enamel corrosion mechanisms the metal material's deterioration was also observed.

3.5 Raman spectroscopy

After analyzing the results of SEM and having matched the corresponding Raman spectra for the obtained results, it can be argued that in the case of sample B cuprite (copper (I) oxide), corrosion products on the surface of the sample were found. This mineral forms isometric crystals with a needle pattern octahedron, confirmed by the SEM observation (Fig. 4). In addition to this, peaks indicate the presence of copper (II)—CuO, or 'tenorite'—a mineral which is extremely rare in nature. The last identified product for the sample B was malachite—Cu₂CO₃(OH)₂. It belongs to the group of carbonates and is widespread. It occurs in dense clusters to form dark brown coatings and raids, and also confirmed the SEM observations.

For sample D, only one measurement of the green powder was performed because the corrosion product was on the whole surface of the sample and the solution. The

products that have been identified are: atacamite—Cu₂Cl(OH)₃ and eriochalcite—CuCl₂·2H₂O. The first one belongs to the group of halides. It is perfectly pointed; the crystals are green, have a diamond shine and crystallized in a rhombic pattern. This mineral occurs in clusters, is needle-like and is clearly visible under the scanning electron microscope (Fig. 4). This was shown to be an eriochalcite crystallized ortho-rhombic system, a rare mineral which has a greenish-blue color.

Raman spectra measurements of the metal substrate for the sample E found copper oxide CuO-tenorite and malachite—Cu₂CO₃(OH)₂. Measurements closer to the enamel showed that at around 300 cm⁻¹ a peak is presented, which is characteristic for hydrated glass. In addition, the peaks for the Si–O bonding and the area of the silica are evident. A peak at 2,900 cm⁻¹ was recorded, providing evidence of the presence of K⁺ HCOO⁻. This is very important and indicates the occurrence of a reaction between formaldehyde and potassium ions leached from the glass. The spectrum shows polymerization of enamel which has confirmed glass aging [20]. Modifications are confirmed by the presence of peaks in the area of 1,500 cm⁻¹. Raman spectrum of organic compounds is very complex, for example creating formates active in the area of 2,000–3,000 cm⁻¹.

The analyses for sample F showed the presence of malachite—Cu₂CO₃(OH)₂ and copper oxide CuO-tenorite. Malachite is a mineral, which often finds itself contaminating silicon and calcium. This was confirmed by SEM analysis, which showed the presence of these elements. The values of the peaks and the shape of the Raman spectrum indicate the presence of zinc oxide (mineral form: zincite) and hydrated zinc sulfate ZnSO₄·6H₂O (mineral form: biankit). In addition to this, several peaks were found which would indicate the presence of gypsum CaSO₄·2H₂O. A microscopic (SEM) picture provided proof of this result.

4 Conclusion

Macroscopic and microscopic observations provided information about the intensity of the processes. In an environment of hydrochloric acid (0.1 and 0.01 M HCl) applied to samples: A and D, it is clear that the band made of brass and copper is not resistant and undergoes a process of dissolving, forming deposits on the surface of glass, on the metal and between the materials. In addition, tarnished glass was observed, especially in samples B and C, which were immersed in water. As a result of corrosion of the enamel in formaldehyde, clear cracks appeared on the blue enamel with small white deposits between those materials.

A sensor sample of Limoges enamel on copper (sample E) has distinct corrosive changes. Enamel applied on the metal substrate disconnected after 76 days of induced corrosion. This indicates how intense the effects of formaldehyde are on the object, glass–copper. As a result, the appearance of cracks and holes was rapid at the edge of a superficial layer of enamel as a result of the detachment of vitreous material (enamel). Another way to facilitate the penetration can lead to a way for the heat treatment of the glass enamel. In the case of poorly chosen temperature parameters, weak adhesion strength between enamel and metal could become apparent, which will promote more rapid penetration of corrosive media upon the glass object. Equally important in the acceleration of this phenomenon is the enamel's preparation and careful selection of the composition—including the use of a specific surface material. In this case, copperplate. The results illustrate as to how damaging the presence of organic matter can be on stored glass–metal objects. Unfortunately, they are still used in museum display cases of fiberboard, which will inevitably lead to this kind of corrosive mechanism.

The study identified an aggressive environment affecting the glass sensor replicating an eighteenth century glass-type beaker and fifteenth century enamel from Limoges, in combination with various metals. As for the glass sensors, most chemical and physical changes occur during their storage in an aqueous medium. This is explained by the occurrence of hydration, hydrolysis and leaching. Glass becomes slightly matted with its surface covered with silica gel; thereby acting as a catalyst by activating the reactions with the environment. Formaldehyde causes some structural defects in glass and the COOH^- ions easily combine with leached potassium ions K^+ , forming a crystallized deposit on the surface of the glass.

Storing a variety of connected materials is important when remembering to create the optimal conditions for the two constituent materials. The parameters for storing glass objects connected of two (or more) materials must be very well matched to avoid developing corrosion on one or two components. Usually the weakest began the deterioration

process. Glass does not like to be kept in or near moisture, and the metal is very sensitive to chlorides. Organic material is harmful to both types of materials and sulfates cause the formation of deposits on the surface (such as gypsum). The study also showed the effect of an elevated temperature, which initiates a chemical degradation process.

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