The Influence of Selected Organic Compounds on the Corrosion of Historical Glass Based on Their State of Preservation

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The aim of this study was to investigate the influence of selected organic compounds such as acetic acid and formaldehyde on the historical glass objects of corrosion processes. This is a very important problem for the field of conservation and restoration of glass of art. Glass objects exhibited in museum display cases can be suffered by evaporating organic compounds which undergo to reaction with leached glass elements to create corrosion deposit on their surface. The proposed method called glass sensors has been used to identify results of impact of various external factors on the tested glass. Due to aggressive environment for the objects there created corrosion phenomena. Glass sensor were prepared as reproduced XVIII-cent. materials. The current studies were carried out by modern physico-chemical methods such as optical, metallography, scanning electron microscopy, inductively coupled plasma mass spectrometry and the Fourier transform infrared spectrometry. These techniques allow to determine the composition of the corrosion layers as well as their structure. The issues raised in this work have been studied following an interdisciplinary approach. The information obtained by using different techniques provides a valuable source of knowledge about the chemical reactions taking place on the surface of the glass. The results derived from this work are useful for the design and implementation of exhibition recommendations and better planning of conservation tasks.

1. Introduction

Nowadays, our extremely fast-growing and progressive civilization generates a number of threats to historic objects made of glass. This is due to primarily to environmental pollution and the emission of harmful substances and compounds that affect these cultural heritage objects. At the same time, current research methods and techniques are aimed at preventing and minimizing these harmful effects sometimes observed on the glass objects.

The storage and maintenance of works of art is an important problem since future generations may not be able to enjoy and experience these collections. Therefore, it is necessary to maintain suitable conditions for storage and display of cultural heritage objects. In addition, it is essential to examine the objects in a comprehensive way with the aim of assessing their condition and the proper methods to preserve their maintenance.

The storage and exhibition conditions have a decisive impact on the behaviour of the objects. If the environmental parameters are not controlled, they can contribute to their degradation and deterioration [1]. Glass objects can experience corrosion processes if exposed to large fluctuations in temperature and relative humidity as well as to high light levels. Moreover the presence of organic compounds such as acetic acid and formaldehyde in very local glass surrounding, can accelerate the corrosion process. Therefore, it is very important to have optimal conditions for each object to extend its durability, while reducing its vulnerability to corrosion processes. Cultural heritage objects must not be subjected to damage because of their unique nature. That is why their amount for testing is very limited or mostly impossible.

Glass is well known material for centuries that has provided evidence about quality of life and progress of civilization. Generally, it is classified as a material showing fairly good stability, but this feature is closely related to glass composition and to the storage conditions. Certainly, it is necessary to understand the glass surface and the adverse chemical reactions causing corrosion. Glass corrosion depends on a number of factors including the chemical composition of the glass at the surface, the presence of micro-heterogeneities, the glass structure, the age of the object, the influence of chemical substances present in the environment, and the surrounding temperature. All forms of temperature gradients, poorly chosen air-conditioning and luck ventilation of rooms, and exposure to harmful environment provide favourable conditions for the degradation of the objects. Other important factors that can accelerate the degradation include microorganisms, sunlight, dust, or not suitable humidity.

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The thermodynamic instability of glass, which is in fact a non-crystalline material, is another important factor. At higher temperatures, the glass may even become brittle and cloudy [2].

Glass is a material that has static fatigue, which manifests as a reduction in strength with time. This fatigue can also be produced as a result of the traffic loads and by the action of water or even higher humidity, which can aid in the formation of micro-cracks. The strength of the material remains constant after a certain time, but never decreases to zero. The strength of glass is also dependent on its chemical composition, which can be very diverse and can be influenced by external factors [3]. The condition at the surface also plays an important role in the strength of the glass. It is important to remember that a given object is exposed to various microclimates, which are characteristic of every storage space.

Glass corrosion is a process that occurs on the surface during the first phase and then progresses further attacking and destroying the internal structure. Corrosion products formed during the degradation of the material can behave in two different ways: causing further corrosion or forming a protective (passive) film — as silica gel layer that can provide protection against further corrosion. The process occurs only when an energy barrier known as the activation energy is exceeded. This activation energy can be reached due to the action of light (natural and artificial) and some form of heat [4].

Glass begins to corrode when water sorption takes place at the surface, while the intensity of corrosion depends on the temperature and the chemical composition of the glass. There are three processes occurring on the surface: hydration, hydrolysis, and ion exchange. Hydration involves the transport of water to the interior of the glass structure by diffusion through the micropores, present in the vitreous material [5, 6]. The next process — hydrolysis — occurs as a result of the formation of hydroxyl groups after breakage of metal-oxygen bonds. However, ion exchange where protons replace modifier ions such as sodium (Na+) and potassium (K+) results in a reduction of volume of the surface layer and the formation of cracks in the network [5–7]. All three processes mentioned above may take place simultaneously for glasses with a complex composition. The reaction oxide glass with water is a highly complex process, dependent on the chemical composition of the glass. More likely the material will bind water molecules, specifically in alkaline glasses, which are hygroscopic. In aqueous solutions, the presence of a strong base involves mainly hydroxides and carbonates of calcium, while in the case of glass the alkaline character is formed by oxides of sodium and potassium. It can be stated that the process of corrosion occurs to remove the ion modifiers [6, 8, 9].

Similar to the effect observed for water-soluble salts, a white coating on the surface of a glass is the result of the formation of corrosion products. It appears after a certain period of time, without visible changes. Glass may show defects due to the presence of salts. For example, cracks can be formed due to processes involving abrupt changes in temperature, alteration of the chemical composition of the glass and local pollution. Glass has good resistance to acids because of created silica gel layer, only hydrofluoric acid is excluded. The presence of alkalis and increased temperature accelerates the corrosion processes. The alkaline solution attacks the glass structure immediately resulting in leaching of the alkaline material and breakage of the glass structure [10, 11].

Another negative factor affecting the glass object is the weathering process, which can occur as a result of the interaction among glass and with water (humid) and gases presented in air. The time required to create deleterious damage can be anywhere from a few hours to many years. This process is strongly dependent on composition of glass and very local surrounding components. As a result, new compounds are formed on the surface of the silica gel. The first effect looks like iridescence, because of change optical surface feature and gradually the whole glass surface is coated by white deposit [5, 6, 12].

The aim of this study was to investigate the influence of chosen two organic compounds: acetic acid and formaldehyde on the glass corrosion processes. This problem is a very important issue in the conservation and restoration of cultural heritage objects. This follows from the fact that the glass objects displayed in museum showcases are exposed to the above-mentioned organic compounds causing surface haze, which is clearly observed as a white deposit, after many years of exposing in display cases.

The presence of organic compounds within the display case is particularly interesting if they are considered in relation to these in the immediate vicinity (the so-called background). The source of these types of compounds is specific glue, used for production very stable cheap museum furniture (show-cases) [5, 6, 13].

This research provides an information about the chemical reactions taking place on the surface of the glass. The research results are useful for the design and implementation of exhibitions and for the planning of maintenance tasks for the evaluated objects. In the absence of original historical glass material, the glass sensor method has been applied to identify the influence of various external factors on the corrosion phenomena. Only in this way, sustainable conservation could be predicted. Glass sensor samples were prepared according to an eighteenth-century recipe, which was in accordance with material which was tested by Faculty of Materials Science and Ceramics, which has had signed cooperation with the National Museum in Kraków.

The problem of organic compound has been known for several years in museums. Adverse compounds, found in museum display cases, include formic acid, formaldehyde, and acetic acid. One of these — formaldehyde — has been confirmed by colorimetric analysis after evaluating the atmosphere inside display cases and storage cabinets [6, 7].

Sensors were corroded by induced deterioration process and next tested by different methods. Producing corro-

sion defects have been tested by modern physico-chemical methods such as optical, metallographic, and scanning electron microscopy as well as mass spectrometry with inductively coupled plasma. These methods allow us to determine the morphology and composition of formed corrosion layers, and internal structure. The issues raised by this research are interdisciplinary, while the information derived from the different methods can be used to support the work of conservation specialists [14, 15].

2. Materials and methods

Detailed studies were carried out for samples, called glass sensor, prepared by melted glass with chemical composition closely as possible to the origin one, used in the 18th-century glass production. Therefore, it was possible to carry out a wide range of analysis without interfering with any work of art, only fully studying their corrosion processes. The composition of glass sensor samples prepared in the department laboratory is shown in Table I [14, 16].

TABLE I

The chemical composition of raw glass model samples.

Material	Concentration [wt%]
SiO_2	62.62
K_2CO_3	19.74
$CaCO_3$	13.72
$Na_2B_4O_7 \cdot 10H_2O$	3.34
MgO	0.49
Na_2CO_3	0.27
$BaCO_3$	0.15
Al_2O_3	0.06
PbO	0.04

Fourteen glass samples were prepared. Half of them were aged by boiling in containers with distilled water for 80 h, and at various time intervals at a temperature 98 °C. Two glass samples (R1 and R2) were used as reference samples. The reference sample denoted R2 was boiled in distilled water, while the sensor R1 has not been exposed to any chemicals. The remained samples were subjected to corrosive environments by placing them in a variety of media. Reference and aged samples were kept in desiccators in order to be exposed to the vapours of selected organic compounds in an attempt to depict the conditions found in museum display cases. Two situations were examined: when the solution is permanently located in a desiccator and when after approximately 1.5 months the solution is replaced with fresh reagents. The amount of solution used was 50 ml and the container was sealed to reduce the escape of vapours [13].

For comparison, another part of samples were kept in separate containers and completely immersed in 50 ml of the chosen media. After 3 weeks, the samples were pre-dried, weighted, photographed, and characterized in detail depending on the capabilities of the currently available analytical methods. A list of the evaluated samples

is presented in Table II. The solutions used were 80% acetic acid and 20% formaldehyde.

TABLE II

List of samples along with their symbols. Samples 1, 3, 5 are aged, and 2, 4, 6 are unaltered.

Corrosive solution	Desiccator		Container
	permanent	change	
formaldehyde	F1	F3	F5
	F2	F4	F6
acetic acid	K1	K3	K5
	K2	K4	K6

Induced corrosion lasted for 162 days during the period five and half months, when the samples were subjected to the selected organic compounds. Suitably prepared samples indicated with R2, F1, F3, F5, K1, K3, K5 were boiled in containers with distilled water for 80 h at various time intervals at a temperature of about 98 °C. Samples were periodically removed from the containers and weighed (R1 has not been corroded in water) [12, 17–21].

3. Results

3.1. Optical microscopy

The surface condition of the glass samples was subjected to induced corrosion in various media and observations were carried out using an optical microscope. In this way it was possible to characterize the corrosion products.

Reference samples R1 (unaltered) and R2 (sample boiled in distilled water for 80 h) were not been exposed to the organic compounds. In the case of aged samples, deposits were observed on the surface of the sanded glass, while no changes were detected for the unpolished surface.

The higher intensity of dust has been located in hollows, grooves and the area behaves like a polished surface and was found without changes caused by boiling process of the samples [22].

The following aged samples were exposed to formaldehyde: F1 — kept in a desiccator, F3 — placed in the fumes of the test compound, and F5 — located in a container with the corrosive solution. Observations by a magnifying glass of these samples showed no significant differences. For each sample, the emergence of more intensive white dust on the surface at the intersection of the glass has been confirmed. The deposit of lower intensity was observed for the ungrounded surface and in areas of chipping. In fact, deposits have greater intensity compared to the ground surface. The longer time of reaction, the more intensity of creating white deposits. Corrosion products were more visible on the sample corroded in the whole solution volume of formaldehyde. In addition, an increased number of cracks were visible on the surface.
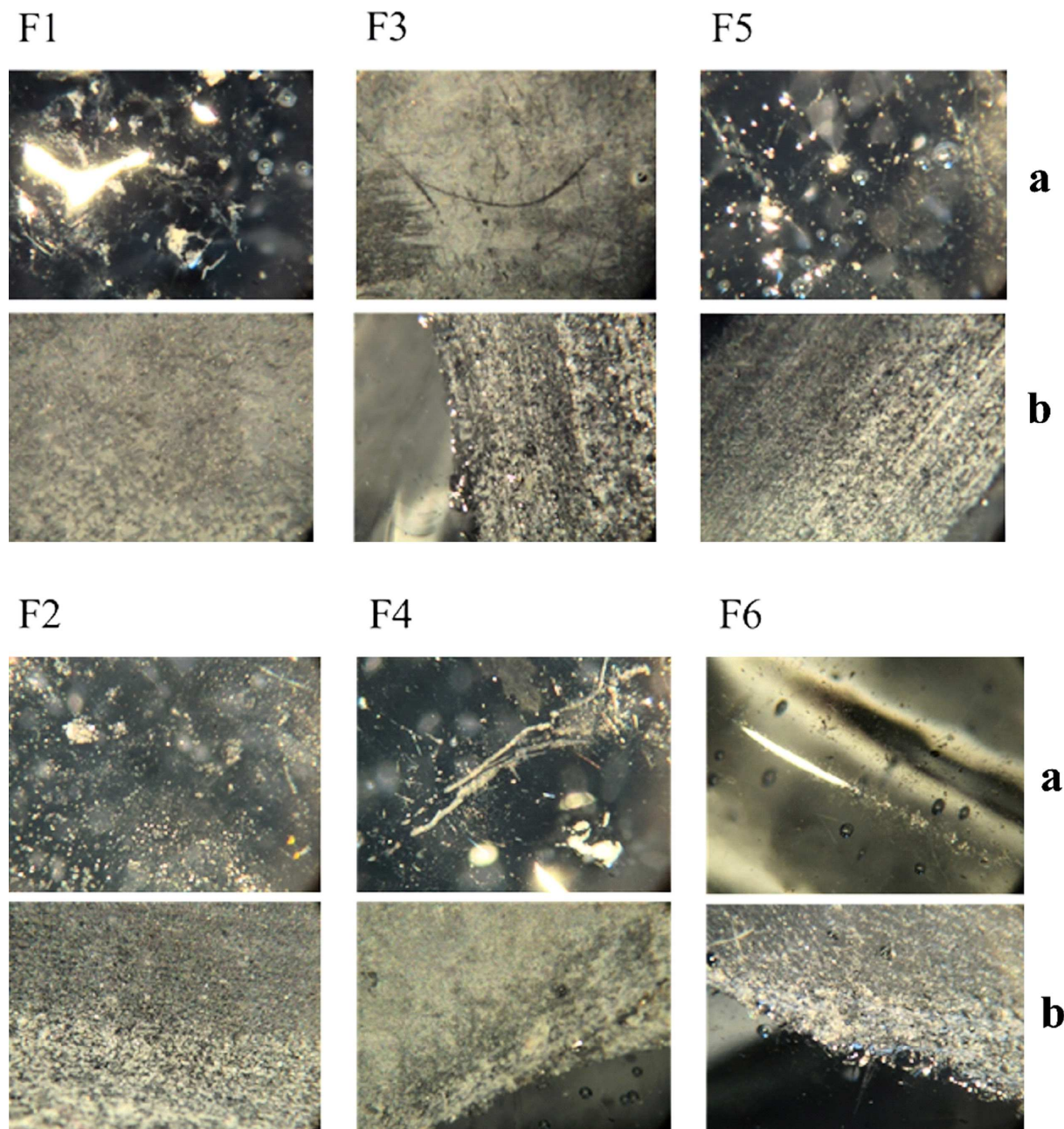
Fig. 1.   Pictures from metallurgical microscopy for samples from F1 to F6.

The changes observed for the unaltered samples treated with formaldehyde are less intense than those obtained for the aged samples. This situation is observed for both samples: F2 (contained in the fumes when a fresh aliquot of formaldehyde is used), F4 (contained in the fumes without replacement of the solution), and F6 (kept in a sample solution container). There should be emphasized a special situation on the sample F2. It presented an orange bloom due to the expansion of the metal ions on the sample, and air black residue resulting from the glass fibre mesh. For ungrounded surface, no changes are observed relative to the surface of the glass. On the other hand, in the "recesses", the intensity of the white staining is stronger than that observed for the ground on

polished surface, but weaker for the aged samples. For the sample kept only in formaldehyde vapour (F4) by 150 days, induced corrosion cracks appeared on one of the walls.

Considered glass samples can be characterized as follows: K1 (aged) and K2 (unaltered) sample kept in a desiccator with a replacement solution of acetic acid, K3 (aged) and K4 (unaltered) sample kept in the acetic acid vapour and finally K5 (aged) and K6 (unaltered) immersed in the container with the same corrosive solution.

Glass samples treated by acetic acid are covered by the white coating. It is much weaker than the one observed for samples exposed to a corrosive solution of formaldehyde.
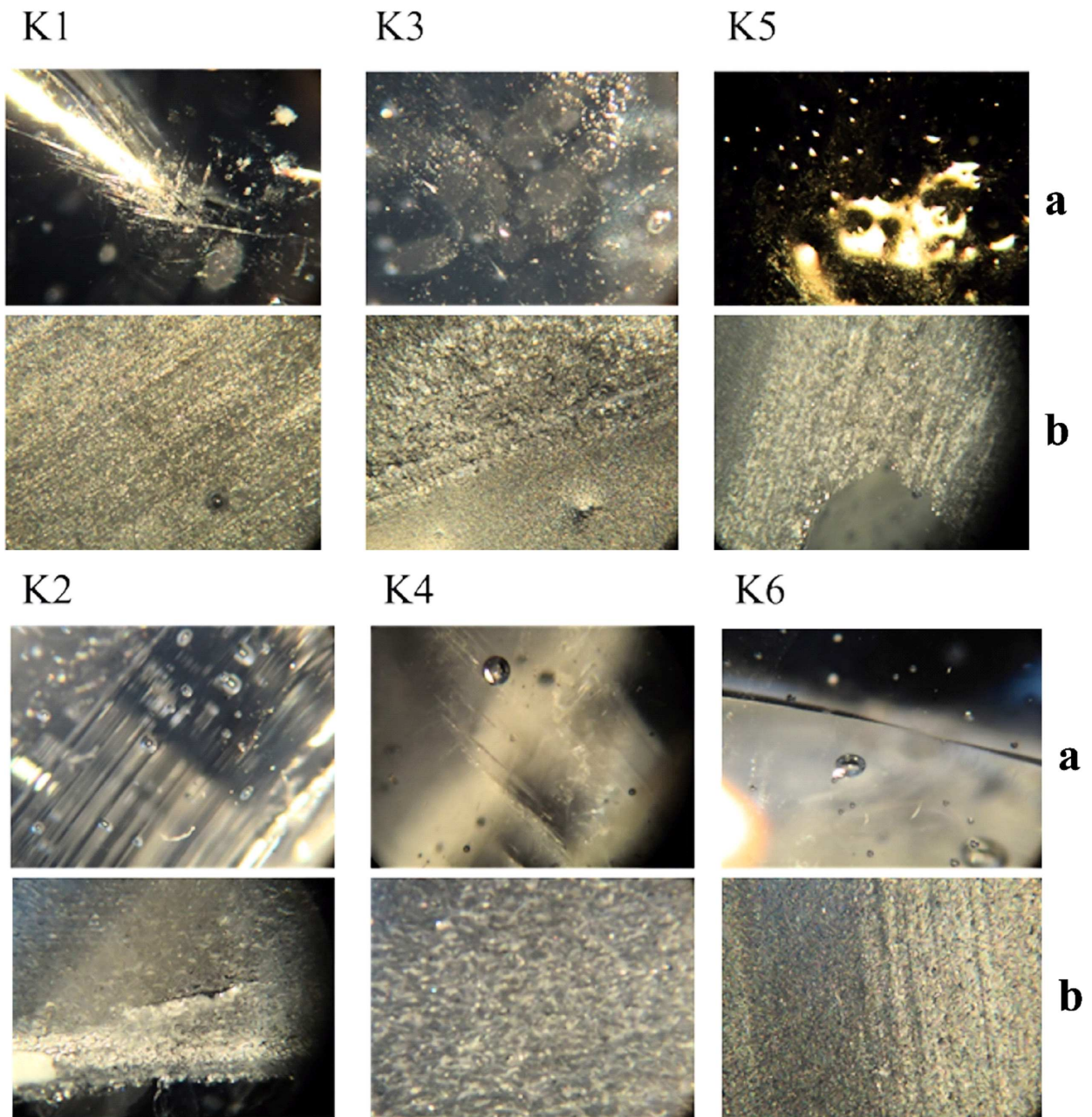
Fig. 2.   Pictures from metallurgical microscopy for samples from K1 to K6.

In addition, the polished surface of the recesses has a faster rate than that of the deposit ungrounded surface. Aged samples have been corroded for longer time. Observations by magnifying glass, pointed greater deterioration in relation to the unaltered samples.

The unaltered sample K2, which was located in the vapour of acetic acid showed a crack in one of the walls and was widened due to the influence of the acid. Sample K4 revealed the appearance of streaks on the surface of the glass. In each of the cases, the longer the time, the bigger the corrosion effect accompanied by an increase of white efflorescence. It was realized due to activity of very weak acid. But in spite of this activity time of corrosive media is a very important factor [23, 24].

3.2. Metallographic microscope

After approximately 30 day induced corrosion, glass sensors were tested by metallographic microscope. Visible changes due to corrosion refer to all presented cases, especially in the grounded surfaces. In contrast, unaltered glass show numerous blisters as a result of corrosion. Microscopic observations revealed the occurrence of cracks in some cases, and also surface scratches on the test samples.

The tested samples also showed defects and inhomogeneity in their structures, such as blistering or losses. Overall, it is worth noting the differences in the surface structure of the ground and uncut glass. Corrosion products are more frequently on the surface of the ground

glass, which is characterized by a greater diversity and inequality. All corrosion processes will occur more easily in places that where mechanically tampered within the structure of the glass [3, 4, 25].

Visible corrosive changes have appeared almost on all the samples. They are displayed on the grounded surfaces. Unaltered surface has more bubbles and looks like an unaltered one. Microscopic observation pointed more cracks and scratches which are shown in Fig. 1 and Fig. 2. There are presented pictures: from F1 to F6 and from K1 to K6, where letter "a" refers to surface before corrosion, and "b" surface after corrosion [25].

3.3. Scanning electron microscope with energy dispersive X-ray spectrometry

Consequently, after each stage of corrosion, the surface morphology was examined by scanning electron microscope (SEM), but semiquantitative chemical composition of chosen surface points was analyzed by energy dispersive X-ray spectroscopy (EDS).

EDS analysis for unaltered reference sample R1 confirmed the presence of silicon dioxide and alkali. This is consistent with the model of melted glass composition. Analogously, measurements were also performed for the reference sample R2, which was boiled in distilled water. Obtained results are presented in Table III. After comparing with the aged sample, a lower sodium concentration was observed in the spectrum. This may be resulting from the occurrence of hydrolysis and hydration reactions. This is a phenomenon that causes leaching of alkali from the glass, resulting in sodium ions moving into the solution, where they will undergo further reactions. An intense band of oxygen and silicon observed in the EDS spectra confirmed the formation of a gel layer on the sensor glass surface due to the adsorption of water initiating the corrosion reactions and alkali leaching.

In order to illustrate the effect of various organic compounds (formaldehyde, acetic acid) on the corrosion process, a test was performed using glass sensors, too. Glass sensors were treated with a 20% solution of formaldehyde for 150 days inducing the corrosion [13, 14].

The sample surface of the aged glass sensor was kept in a container containing formaldehyde solution. The destruction of the surface due to its contact with this organic medium caused pitting corrosion. This effect significantly speeds up the corrosion process [16].

The EDS results shown in Table III pointed carbon presentation. Different concentration of carbonate products have been presented on the tested surfaces. SEM analysis was also conducted for unaltered glass sample (F6), which was kept in the formaldehyde solution.

SEM observations confirmed less surface changes than these ones observed on the surface of aged glass sensor. This is due to the fact that the sample was unaltered, with water at elevated temperature. These results pointed higher resistance to corrosion caused by the organic compounds. The increased content of carbon and oxygen is likely to indicate the oxidation of formaldehyde
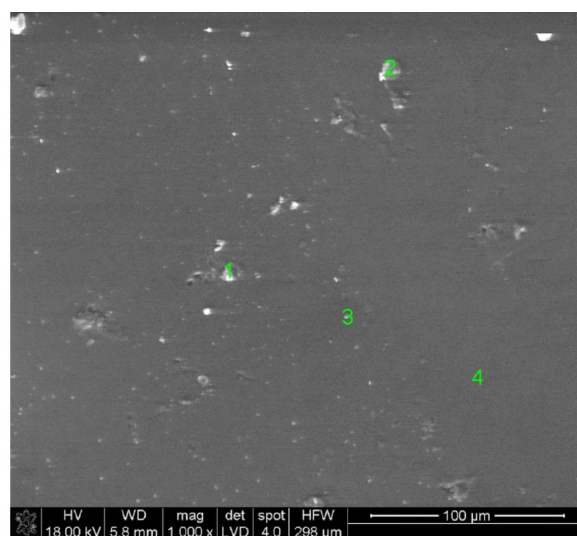

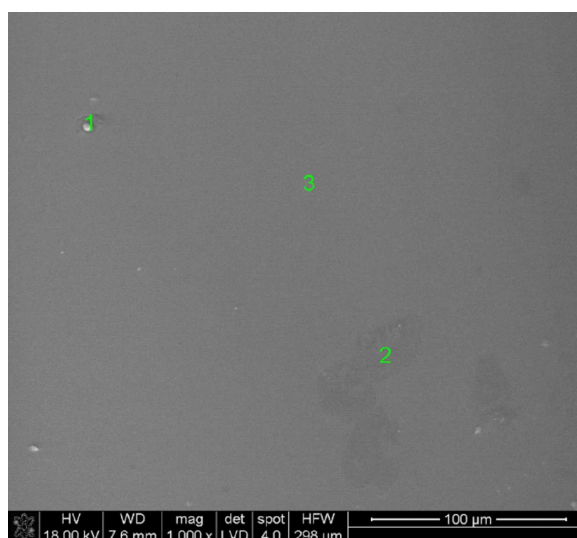Fig. 3.   SEM analysis for aged sample K5.

Fig. 4.   SEM analysis for unaltered sample K6.

into formic acid, followed by the reactions with the alkali in the glass.

The samples were kept at all times in the corrosive organic solution. Due to this, formaldehyde was carbon source. This compound produced a haze area and a precipitate on the walls of the glass sensor. Observation surface by SEM pointed intense band of silicon, due to created silica gel layer. Information from carried out analyses showed the diversity of the surface and also formation of heterogeneous process of dealkalization [15, 22, 24].

The analysis for samples: K5 (aged) and K6 (unaltered) interacting with acetic acid, were performed using SEM as well as EDS methods. Corrosion products had irregular shapes, probably derived from carbonates. Samples treated with acetic acid were analyzed in several areas. A fairly high carbon content was the result of keeping the samples in an organic solution.

The sample K6, without ageing process, has been exposed in acetic acid solution and showed some early signs

TABLE III

Chemical composition of corroded samples (EDS).

	Concentration [wt%] in sample					
	F1	F2	F3	F4	F5	F6
C	43.890	18.340	39.357	6.473	36.817	5.930
O	23.403	40.058	23.820	41.650	30.623	40.237
Na	0.527	0.955	0.490	1.457	1.243	0.513
Mg	0.330	0.530	0.290	0.500	0.430	0.630
Al	0.273	0.488	0.477	0.413	0.350	0.470
Si	18.933	27.595	24.327	28.370	20.657	36.570
P	0.160	0.245	0.143	0.143	0.127	0.190
S	0.287	0.305	0.000	0.140	0.223	0.197
Cl	0.217	0.223	0.097	3.773	0.000	0.153
K	4.550	7.050	7.197	12.820	6.293	9.587
Ca	4.433	4.208	3.800	4.263	3.233	5.523
C	8.010	3.953	28.460	4.358	13.075	6.280
O	36.193	40.263	30.853	33.960	39.320	33.650
Na	0.807	1.273	0.773	1.220	1.080	0.397
Mg	0.377	0.600	0.430	0.558	0.345	0.220
Al	0.483	0.570	0.485	0.485	0.520	0.197
Si	34.863	35.523	23.368	37.030	30.130	37.677
P	0.237	0.140	0.165	0.218	0.145	0.000
S	0.227	0.273	0.755	0.333	0.335	0.000
Cl	0.433	0.268	0.383	0.358	0.305	0.197
K	12.237	10.910	8.013	14.150	9.800	14.230
Ca	6.133	6.233	6.320	7.333	4.955	7.163
	R1			R2		
C	32.706			33.760		
O	33.991			26.900		
Na	1.340			1.150		
Mg	0.370			0.345		
Al	0.407			0.385		
Si	18.524			18.255		
P	0.171			0.000		
S	0.244			4.385		
Cl	3.346			0.000		
K	7.147			6.415		
Ca	2.717			8.405		

of corrosion as well as the presence of weak organic corrosion products, as presented in Fig. 3 and Fig. 4.

The presence of carbon in the case of the glass sensors can have two sources. Carbon can be derived also from the organic solution and tiny amount from calcium carbonate used as a raw material, subjected for melting. In addition, the current studies have confirmed the formation of a white precipitate crystals on the surface of the analyzed glasses — Table III [7, 16].

3.4. Inductively coupled plasma-mass spectrometry

In the next stage of research, the corrosion of the glass sensor samples were measured by inductively coupled plasma-mass spectrometry (ICP-MS). The corrosive solutions: acetic acid and formaldehyde were tested after corrosion process for sample K5, K6, F5, F6. Acetic acid was medium for corrosion aged K5 and unaltered K6.

But formaldehyde was for aged F5 and unaltered sample F6. All these material was analyzed by ICP-MS. Glass sensors K5 and K6 were immersed in acetic acid but F5 and F6 were in formaldehyde. Obtained results are summarized in Tables IV and V.

TABLE IV

Summary of the results obtained using the ICP-MS spectrometry for corrosive media acetic acid (samples K5 and K6) and formaldehyde (samples F5 and F6).

	Concentration [mg/L] in sample			
	K5	K6	F5	F6
Ca	849.65121	852.09822	14.44589	9.92743
K	1.22388	1.36472	0.22772	0.40722
Mg	21.36209	20.95239	0.48087	0.35603
Na	3.18916	3.09549	0.88218	0.89851

TABLE V

Summary of the ratios obtained for the acetic acid samples (K5 and K6) and the formaldehyde samples (F5 and F6) for chosen elements.

	Ratio in sample			
	K5	K6	F5	F6
Ca/Si	253.3	265.4	61.2	39.4
Si/K	2.7	2.4	1.0	0.6
Si/Na	1.1	1.0	0.3	0.3
Si/(Na+K)	0.8	0.7	0.2	0.2

Obtained results indicated created leaching phenomena. This is especially noticeable in the case of corrosion in acetic acid, compared with dealkalization in formaldehyde where the concentrations of calcium, sodium and potassium were much lower. The acetic acid caused the formation of a gel layer. But due to the acid vapors activity some amount of alkali can move from the glass to the solution. In the case of formaldehyde, a smaller content of the elements under consideration was observed due to the formation of white cast on the glass surface. The situation is complicated mainly due to that the chemistry of the corrosion process caused interaction between the acid with the aldehyde. Formaldehyde does not react so intensely by its very nature. However, in an aqueous environment it will not react directly with the glass, but with the alkali leached from the glass, to form alkali formates. A large part of created formates were precipitated, but some part were depolymerizated.

There was a very high concentration of calcium ions in the solution of acetic acid indicating the passage of the elements to surrounding of the glass sensor. The concentration of elements such as sodium, magnesium, potassium and silicon recorded by the ICP-MS were a result of increased leaching of the alkali from the sensor samples due to ion exchange, even in the case of acetic acid with respect to formaldehyde. It is well known that the glass is subject to hydration phenomena, leaching, and also hydrolysis under the presence of water [4, 6, 7]. The contents of the respective elements, which have been mentioned previously show that this phenomenon has ap-

peared. After analyzing the data contained in Tables IV and V, in relation to the elements there is no distinction between samples within a corrosive medium. The unaltered samples as well as the treated ones behave similarly, when formaldehyde is used. In the case of acetic acid with strong concentration, due to high acid hydroscopy, obtained data are in contrast to formaldehyde activity. This property is responsible for the absorption of moisture and due to this leads to dissolution of created small alkali acetates.

3.5. The Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was used to define the kind of corrosion processes of bulk glass of glass sensor samples. They were exposed to aqueous formaldehyde solutions (F5) and concentrated acetic acid (K5) too. FTIR spectra of the corroded samples referred to the bulk glass are shown in Fig. 5.
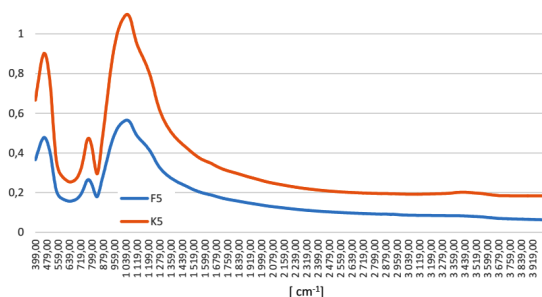

Fig. 5. FTIR spectra of samples K5 and F5.

For both registered spectra, bands at 1040 and 770 cm^{-1} belong to the glass structure. At higher wavelengths, no bands were observed.

At around 1040 cm^{-1}, a band with the form of a doublet silica–oxygen is observed in both spectra. It means that formaldehyde interacts only with silicone layer, but not structure. It was confirmed by the stretching Si–O vibration at around 1040 cm^{-1}. Surface degradation occurs accompanied by the formation of a white product but only on the surface. Due to the ongoing reactions, a salt derived from organic compounds reacts with leached elements glass surface. The leached layer rich in SiO_2, showing lack of alkali, is similar to the silica gel-layer structure. Analyzed bulk glass has not visible structure changes.

4. Results and discussion

The main aim of this study was to investigate the influence of two organic compounds, 20% formaldehyde and 80% acetic acid on the historical glass sensor of corrosion processes. Organic compounds have been proved in museum display cases. Organic substances were emitted from chipped board, used to make museum exposition furniture. Consequently, many XVIIIth c. glasses have been destroyed due to corrosion process. Because of lack the original material, glass sensors were done for the XVIIIth c. original object. The observations and information recorded during the progressive corrosion helped to better understand these changes.

The study involved analysis of corrosion under the influence of the various reagents in the case when the samples were pre-aged by their boiling in distilled water. The prepared samples interacted with the selected organic compounds for the entire period of induced corrosion. The samples were kept at room temperature in conditions similar to museum circumstances used for the exhibition of historic objects made of glass. The weight of individual samples was periodically monitored. The samples were also photographed and any changes were reported.

Studies were carried out by analytical methods, which included: metallographic, and scanning electron microscopy SEM with EDS, mass spectrometry with inductively coupled plasma ICP-MS, and FTIR. Some observed analyzed samples showed the appearance of white surface spots, which were especially visible on the ground surfaces. They refer to corroded (aged) glass, for example, from museum or excavation activity. In addition, the formation of corrosion products grew gradually with increasing duration of induced corrosion.

The biggest changes in the examined glass sensor samples occurred during their entire immersion in the aquatic environment, which was related to the phenomenon of overlapping hydration, hydrolysis and leaching. Due to the this, dealkalization was created and proved by SEM and EDS. The sample surface is covered with the silica gel. Some amount of leached alkali from glass comes to reaction with carboxyl group COOH–, originating from formaldehyde. Due to this phenomenon, created new products — salt (alkali formates) — covered glass surface, as a corrosion product.

Because harmful formaldehyde activity caused coating of the whole surface area, significant changes on a glass surface have been created. This was confirmed by the SEM images. The surfaces of these samples were characterized by the presence of pits, which allowed the penetration glass material by corrosive media.

As previously mentioned, the main problem was the formation of the corrosion product, which is present as a white coating layer. This refers to both media: the acetic acid and the formaldehyde [3, 7]. In both cases the formation of salts of these compounds was confirmed by EDS results. Organic compounds used for making museum display cases usually emitted organic substances which made adverse effect on historic objects.

The carboxylic acids in aqueous solutions of hydroxides allow for the relatively easy formation of the salt, which is a non-volatile crystalline solid. Therefore, the created salts on the surface of the glass sensor samples are soluble in water, causing reduction of their concentration on the glass surface layer. Moreover it caused the transport of alkali from the center to the surface layers of glass. Formaldehyde due to temperature gradients underwent to the new phase — called polymerization, which easily become depolymerization.

It may also occur where the polymerization of the linear polymers is formed. Paraformaldehyde is a

compound existing as a white solid subsequently undergoing the process of dehydration.

As a result of various reactions there can occur oxidation of formaldehyde into the corresponding acid or acetic acid reduction to the aldehyde. In the present system, it may also arise from the combination of two molecules through the creation of hydrogen bonds, which change the properties of the resulting product.

To make statistical comparisons of composition of the glass sensor before and after the induced corrosion statistical tests should be done. Due to very limited number of samples, the statistical assessment was impossible for this research. The next part of tested glass sensor is proposed. Obtained data would be helpful to verify differences among obtained values and to get more information on corrosion processes.

The glass sensor method is shown to be very useful application for indicating the adverse products affecting historic objects. Moreover, glass sensors can be used to monitor local environment. The presented research allowed to obtain information about the influence of the organic induced corrosion processes on glass. The use of the glass sensors eliminates the need of employing specific objects and at the same the results can be correlated to data, expected from analysis of real museum objects.

5. Conclusions

On the basis of the study it can be concluded that:

- the presence of organic compounds in storage cabinets and exhibition cases proved to be very harmful factor for glass objects;

- the glass sensor method is possible to induce glass corrosion in a variety of media.

- corrosion-induced tests allowed confirming the reactions of historical glasses with organic compounds, pointed their influence on depending of their intensity;

- the induced corrosion tests on aged samples confirm dependence on object stage on monument stability;

- the degree of degradation of the glass clearly reveals the changed of surface morphology of the aged and the corroded sample immersed in corrosive media;

- these kind of studies can be used to better execution of restoration works of historical objects in museums and they can provide valuable information about the corrosion processes resulting from the evaporation of organic compounds and their action on the historical objects;

- FTIR data proved dependence time of corrosion activity on glass.

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