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EFFECTS OF EMISSIONS OF MATERIALS FOR WRAPPING, TRANSPORTATION AND STORAGE ON STAINED GLASS WINDOWS AND ON GLASS OBJECTS IN SHOW CASES IN MUSEUMS

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ABSTRACT

The emission of volatile organic compounds (VOC) of materials for wrapping, transportation and storage of stained glass windows were investigated by direct thermal desorption. The analysis was performed with thermal desorption in combination with gas chromatography and mass spectrometry. Emissions of organic acids were determined. The damage risk of volatile organic compounds, e.g. organic acids as acetic acid, propanoic acid, hexanoic acid and octanoic acid was investigated on model glasses in climate chambers. After exposure the surface of the most sensitive samples was damaged.

Based on emission measurements in exhibit cases of the former museum "Grünes Gewölbe in the Albertinum" in Dresden, Germany, the atmospheric conditions inside the show cases were determined. It can be shown that the atmospheric conditions inside the cases endanger the glass and enamel objects of art especially in show cases with low air exchange rates. Materials with high emission rates of organic acids should not be in direct contact with medieval glass for a long time and should not be used in exhibit cases. Acid emissions, especially acetic acid plays an important role during investigation of different materials for show cases and can be determined by direct thermal desorption.

BACKGROUND

Medieval stained glass windows can be damaged by the action of inorganic and organic pollutants in the air. The effect of air pollutants comprising industrial fumes and moisture acting as acid rain on the stained glass windows of churches and cathedrals is well known. However, emissions from materials used for wrapping, transport and storage of glass art objects can also damage these sensitive materials[1]. Chemical reactions of poorly resistant medieval glass with ambient vapours and gases lead to an alteration of the near surface region of the glass, paint layers and lead and to formation of corrosion crusts. The high sensitivity of medieval glass is caused by their chemical composition.

There are also known damage phenomena on glass and enamel objects of art in show cases. Show cases are usually necessary to protect cultural objects from theft as well from dust and mechanical damage. But sometimes the atmospheric conditions inside the cases endanger the objects, especially in show cases with low air exchange rates. Therefore materials for presentation and storage of historic glass objects must be tested for emissions of volatile organic compounds before application to avoid damage of the objects.

ANALYSIS

The emission of volatile organic compounds from materials for wrapping, transportation and storage of stained glass windows were investigated by direct thermal desorption. The materials were made available by restoration departments and glass museums. Analysis was performed with thermal desorption in combination with gas chromatography and mass spectrometry.

Direct thermal desorption is a fast and easy method to identify possible material emissions. Volatile and semi-volatile organic compounds (VOC and SVOC) can be detected from very small-sized samples of material (0,001-0,02 g).

Material	Material
particle board No.1	pine wood
particle board No.2	hardboard
styrofoam/polystyrene	bubble wrap
foam/cellular material	wood shavings
ethafoam	cappa carton
wrapping tissue No. 6	wrapping tissue No. 7
corrugated cardboard	newsprint
Biopac	Ecopac
cardboard box	blockboard, coreboard

Table 1: Materials for investigation by thermal desorption

Equipment for the investigation: Gerstel Thermal Desorption System TDSA 2 and TDS 3 with Gerstel Cold Injection System CIS 4; Agilent Gasgromatograph with Mass Spectrometric Detector.

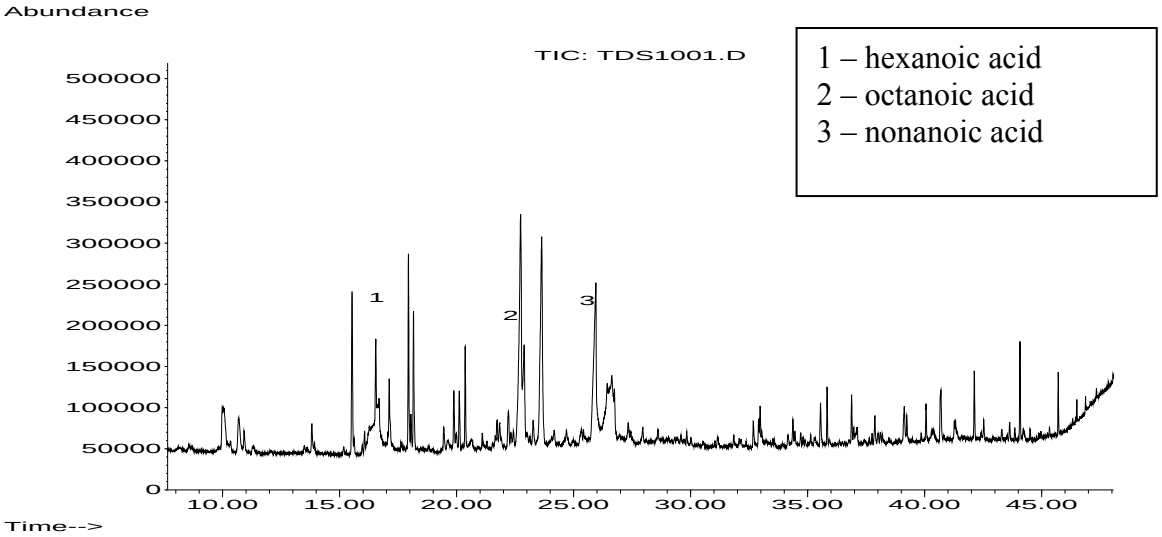

Fig. 1: Gas chromatogram of a sample of pine wood

Emissions of organic acids were determined among other volatile organic compounds.

VOC	Identifikation number CAS
Acetic acid	64-19-7
Propanoic acid	79-09-4
Propylene Glycol	57-55-6
2,3 Butanediol	513-85-9

Acetic acid, methoxy- Anhydride	19500-95-9
Hexanoic acid	142-62-1
Ethanol, 2-(2-ethoxyethoxy)	111-90-0
Nonanal	124-19-6
Hexanoic acid, 2-ethyl-	149-57-5
Ethanol, 2-(2-butoxyethoxy)-	112-34-5
Octanoic acid	127-07-2
Decanal	112-31-2
Ethanol, 2-phenoxy-	122-99-6
Nonanoic acid	112-05-0
Dibenzofuran	132-64-9
Pentadecane	629-62-9
Diethylphtalate	84-66-2
TXIB	6846-50-0
Dodecanoic acid 1-methylester	010233-13-3
Diisopropylnaphtalene	038640-62-9
Octadecane	593-45-3

Table 2: Volatile organic compounds found in samples of foam/cellular material

In three of all material samples organic acids were determined. Organic acids are able to react with glass components and changing the glass surface and stability. The materials were already in use for a long time in glass museums.

Material	**Organic Acid Emission**
foam/cellular material	acetic acid, propanoic acid, hexanoic acid, 2 ethyl-hexanoic acid, octanoic acid, nonanoic acid
pine wood	hexanoic acid, octanoic acid, nonanoic acid
particle board	acetic acid

Table 3: Materials emitting organic acids

EXPERIMENTS

The effect of organic acids on historic stained glass was tested with simulation materials (see table 4) in desiccators and climate chambers. 2 ml of acetic acid, propanoic acid, hexanoic acid and octonoic acid were put in little bottles, closed with Parafilm. The concentration of the organic acids inside the desiccators depended on their vapour pressure.

Number	Na_2O	K_2O	CaO	SiO_2	Al_2O_3	MgO	CoO
MA	-	28	17	50	1,5	3	0,5
NC	14	1	9	70,5	1	4	0,5

MA medieval glass sample; NC 19th century glass sample

Table 4: Composition of glass samples [Weight %]

Different paint layers (red, black) and samples of lead were also tested. After 12 weeks weathering at 40 ^{o} Celsius and 55 % relative humidity in a climate chamber the surface of the samples was analysed by light microscopy.

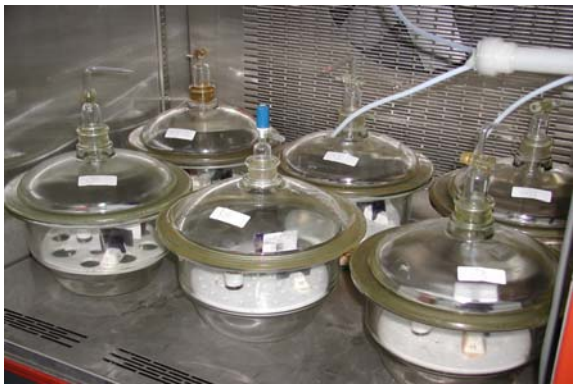

Fig. 2: Desiccators with organic acids and glass samples inside the climate chamber

The assessment of climatic conditions can be achieved by using highly sensitive test glasses as dosimeter materials[2]. Due to its composition, the glass material is very susceptible to leaching and corrosion reactions caused by atmospheric impacts like humidity, rain, temperature changes and acid attacks by pollutant gases. This sensor method can be applied for any kind of artwork material, monitoring the integral atmospherically impact around the object and thus allowing a final risk evaluation. This method, developed at the Fraunhofer ISC, Wuerzburg, Germany for environmental stress monitoring on artwork, has been widely used in many European countries over the last 15 years, especially for monitoring climate effects on stained glass windows[3]. It can also be applied indoors, e.g. in museum display rooms, show cases and magazines[4].

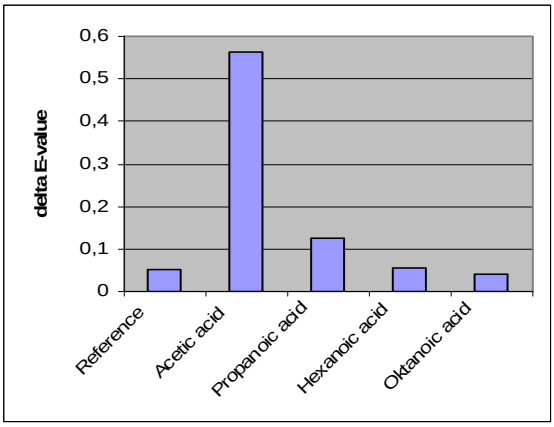

Fig. 3: ΔE-value of organic acids after 12 weeks in desiccators

A distinct value, representing the environmental risk potential (ΔE-value; E: extinction), can finally be stated after instrumental FTIR-analysis (FTIR: Fourier Transform Infra Red

Spectroscopy). The method is certified in Germany as German Technical Guideline VDI 3955/2[5]. The measurements were carried out by Fraunhofer ISC in Wuerzburg.

The higher the ΔE-value the higher is the risk potential for historic glass objects. In this study acetic acid caused the highest value for ΔE (see figure 3).

The surface modification can be seen by light microscopy. It also depends on glass composition (see figures 4 to 7).

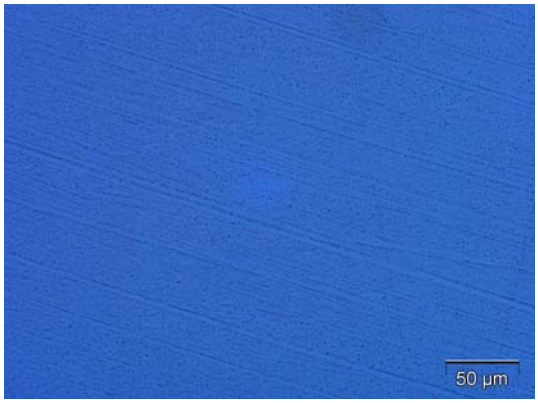

Fig. 4: Glass sample NC affected by 55% r. H.

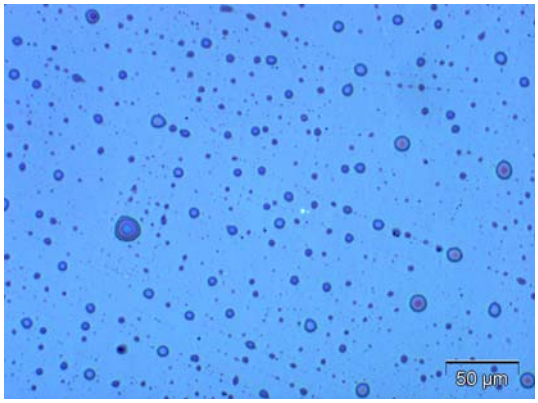

Fig. 5: Glass sample NC affected by 55% r. H. and acetic acid

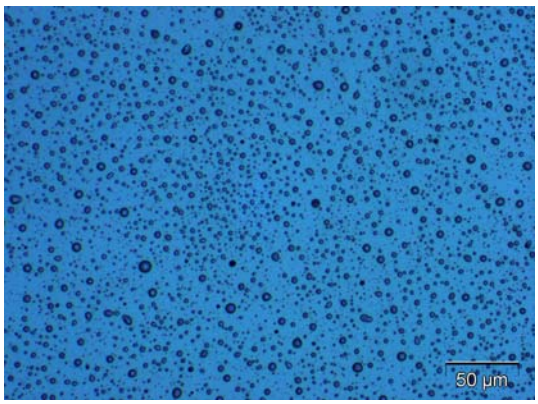

Fig. 6: Glass sample MA affected by 55% r. H.

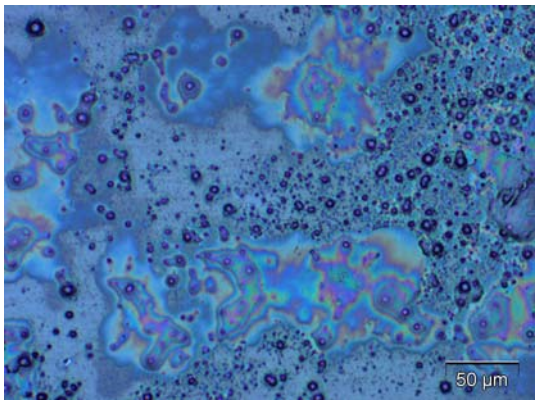

Fig. 7: Glass sample MA affected by 55% r. H. and hexanoic acid

The glass samples with medieval glass composition are more sensitive than 19th century glass samples. Water deposition on the surface of MA-samples can start glass corrosion already (see figure 6). The action of hexanoic acid affects the surface considerably and pits are already seen (see figure 7). The red and black paint layers were also affected by organic acids. On lead surface liquid depositions were observed. The damage by impact of organic acids can be clearly seen. Emissions of acetic acids show the highest damage risk for medieval glass objects.

In this test the concentration of acetic acid in the desiccators was determined by a factor of 10^4 higher than in show cases with a high concentration of volatile organic compounds[6].

In another test the model samples were exposed in desiccators with materials emitting organic acids (see table 3). After 14 weeks in a climate chamber at 40 ^{o} Celsius liquid depositions were observed on the glass surface of MA-samples only (see figure 8, 9). The relative humidity inside the desiccators was about 80 %. The concentration of acetic acid was determined between 400 and 1200 µg/cm^3. After two years exposition at room temperature the cross section of the most affected samples were investigated by scanning electron microscopy (see figure 10). It is known that the glass surface undergoes considerable modifications by different deterioration processes. Organic acids and water on the surface starts an ion exchange process in which alkali- and alkali earth ions from the glass are released into solutions and protons (most probably as H_3O^+ ions) enter the glass to produce a hydrated alkali-deficient surface gel layer. This degradation process can be observed on the surface cross section by scanning electron microscopy.

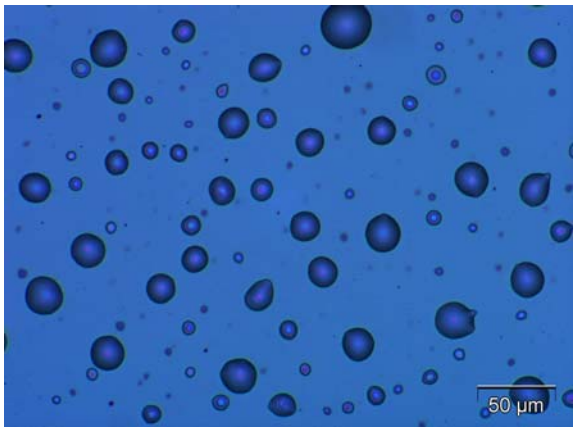

Fig. 8: Glass sample MA affected by emissions of pine wood after 14 weeks

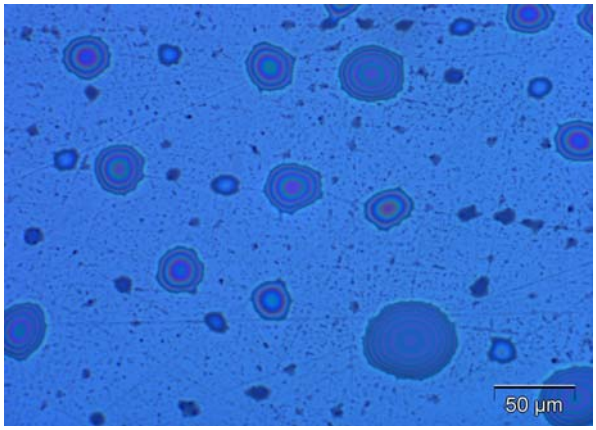

Fig 9: Glass sample MA affected by emissions of particle board/ strand board after 14 weeks

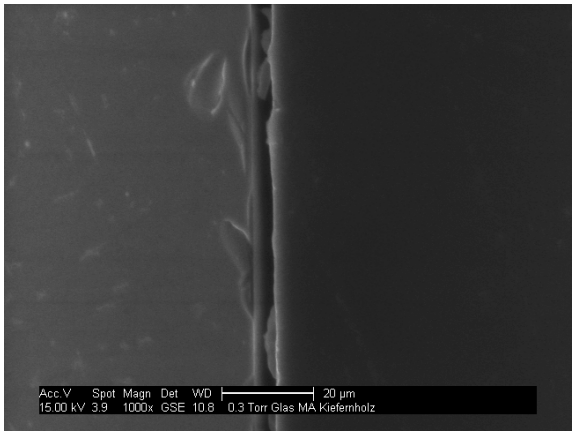

Fig.10: Electron microscope picture of the cross section through glass sample MA after two years affected by emissions of pine wood

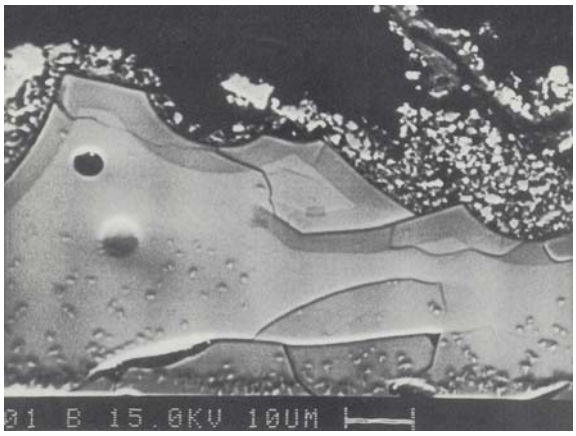

Fig. 11: Electron microscope picture of the cross section through an enamel fragment of an object of art stored in a show case more than 20 years

The samples were embedded in epoxy resin, burnished and polished with diamond paste. In figure 10 the MA-sample is on the left hand side. There are some cracks and flaking of the surface, probably of preparation, but a formation of gel layers is not to be seen. The enamel fragment in figure11 shows gel layers along its surface and indicates the relation between alkali leaching and crack formation. The concentration of acetic acid in the show case where

the enamel objects of art were stored was about 3000 µg/m^3. During a long time deposition loss of adhesion and peeling off of enamel layers from historical art objects were the consequence[6].

SIMULATION

Glass sensors were used to determine the risk potential (ΔE-value) of inorganic and organic emisssions[7]. The experiments were carried out in climate chambers and emission test chambers. The influence of relative humidity was investigated together with sources of inorganic and organic emissions. The weathering took place with SO_2, NO_x (gaseous concentrations) and organic acid emissions. Concentration of acetic acid in the emission test chamber was similar to the concentration measured in a museums show case of about 3000 µg/m^3. In another test a particle board emitting formic acid, acetic acid and formaldehyde was used. The analysis was performed with thermal desorption in combination with gas chromatography and mass spectrometry (GC/MS). After 14 days weathering at 23^o Celsius the ΔE-values of the glass sensors were determined by Fraunhofer ISC, Wuerzburg.

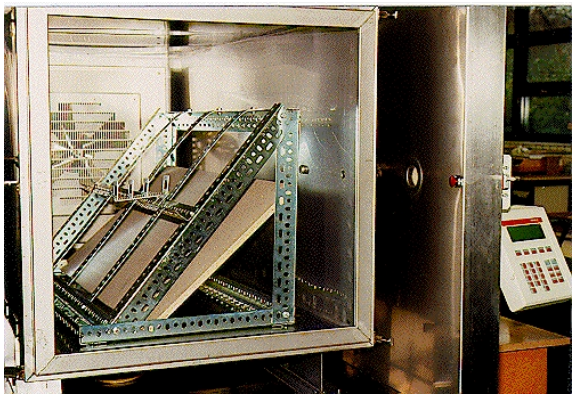

Fig. 12: Glass sensors in an emission test Chamber loaded with particle board

No	T [^{o}C]	r.H. [%]	Inorganic emission concentration [µg/m^3]	Organic emission concentration [µg/m^3]
A	23	55	0.4 SO_2; 51.2 NO_x ; 23.8 O_3	
B	23	55	435.5 SO_2; 6.9 NO_x; 1.4 O_3	
C	23	55		3000 acetic acid
D	23	45		3000 acetic acid
E	23	55		300 acetic acid; 150 formic acid; 200 formaldehyde
F	23	45		150 acetic acid; 50 formic acid; 160 formaldehyde

Table 5: Simulation conditions

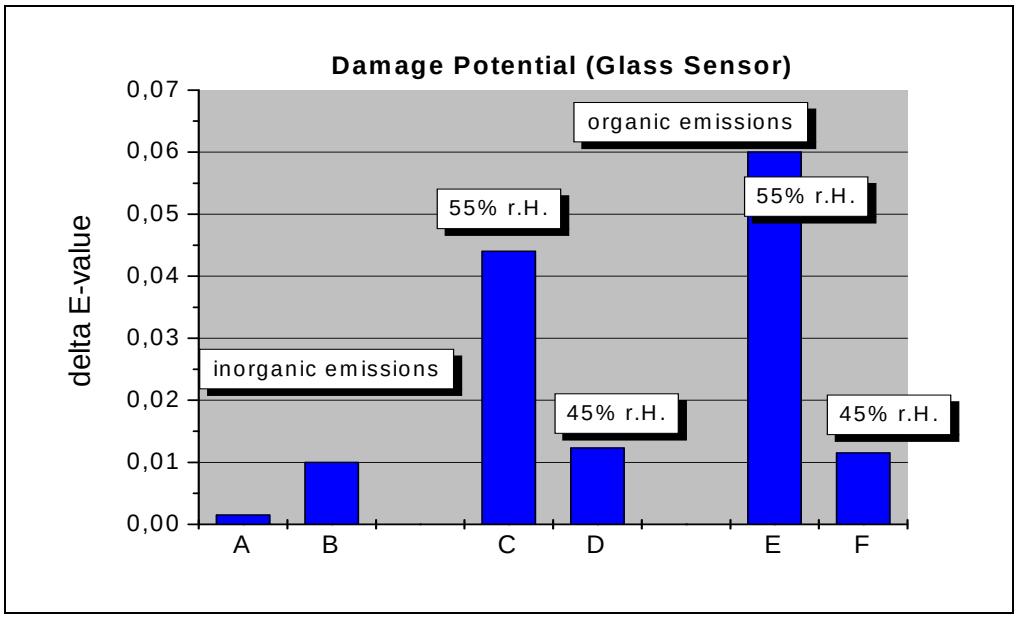

Fig 13: Damage potential of inorganic and organic environmental conditions measured on glass sensors after 2 weeks treatment in climate chambers at 23°C (see Table 5)

Experiment A shows the damage potential of natural environmental conditions on glass sensors. The SO_2 concentration in experiment B is much higher than in industrial areas with high SO_2-emissions. The acetic acid concentration of 3000 µg/m^3 was measured in a show case in a museum and has been reproduced in experiment C. The damage potential of organic emissions on glass sensors is much higher as for inorganic emissions but there is also a big influence of the relative humidity. If the relative humidity is reduced from 55 % to 45 % the ΔE-value decreases considerably (experiment D).

In experiment E a particle board was used as emission source. Synergistic effect of acetic acid, formic acid and formaldehyde caused the highest ΔE-value for the glass sensors. Reduction of the relative humidity from 55 % to 45 % (experiment F) decreased the ΔE-value even more than in experiment D because the reduction of the relative humidity additionally reduced the emission rate of the compounds emitting from the particle board.

CONCLUSIONS

Materials emitting organic acids should not be used for wrapping, transportation and storage of historic glass objects of art for a long time. Organic acid emissions have a higher damage potential than inorganic emissions. The sources of emissions in show cases are construction materials and art objects themselves, for example after restoration and after treatment with chemicals. Therefore it is necessary to investigate materials with direct thermal desorption before use to avoid possible emissions of volatile organic compounds.

Beyond that it can be helpful to increase the air exchange rates inside the show case and archives to lower harmful acid emission concentration. If it is possible, a reduction of relative humidity below 50% is another way to reduce the damage potential of environmental conditions for glass objects of art.

ENDNOTES

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