VOC EMISSIONS FROM CANVAS AND ACETIC ACID DEPOSITION TO CANVAS AND GLASS

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Abstract

The protection of paintings and other objects in collections is a major concern for museum administrators, conservators and national authorities. Artwork may get damaged by accumulation of air pollutants inside protective enclosures due to emissions of volatile and semi-volatile compounds from the exposed objects or from the enclosure itself. Relatively little is known about emissions and deposition of volatile organic compounds (VOC) in the museum environment. We used state-of-the art on-line instrumentation to measure the emissions of small carbonyls (formaldehyde, acetaldehyde, acetone) and carboxylic acids (formic acid, acetic acid, propionic acid) from three different canvas samples provided by the Tate Gallery in London. In addition, we measured the deposition velocity of acetic acid to the three types of canvas and to an activated carbon cloth. In a simple experiment, we confirmed that acetic acid efficiently adsorbs and sticks to establish a layer on a clean glass surface. Finally, we performed a gas chromatographic analysis of a film collected on the inside of a window of a museum exhibition showcase and found a variety of organic compounds including a series of carboxylic acids. Installing and periodically exchanging activated carbon cloths (or other adsorbent media) inside a museum enclosure appears to be an efficient way to reduce volatile organic acid concentrations.

1   Introduction

Acetic acid is emitted from many materials in the indoor environment[1,2]. It is ubiquitously present and often among the most abundant volatile organic gases in indoor air[3,4,5]. The concentration of acetic acid can reach high values inside enclosed spaces with low ventilation such as store rooms, showcases, microclimate frames or transport cases used to protect cultural heritage objects. Acetic acid is corrosive, and it has been found to accelerate the degradation of both inorganic and organic cultural heritage materials and objects[7,8,9,10].

The use of protective enclosures for cultural heritage objects has many advantages. They offer passive physical protection, stabilize the temperature and relative humidity around objects, and protect against external pollutants including particulates. Disadvantages are their weight and cost and the fact that they trap internally emitted pollutants such as acetic acid[6,11]. To prevent damage to objects, the presence of organic acids inside protective enclosures should be reduced while retaining low ventilation to protect against external climate and pollutants. This can be achieved by the use of low emitting construction materials, by sealing emitting surfaces with barriers (e.g. with aluminium foil) or by installing pollutant adsorbers inside the enclosures[6]. It is, however, often difficult to avoid the use of cases made from emitting materials such as wood due to practicality or cost. It is also difficult to quantify emissions from different materials including many types of surface coatings and sealants. The installation of adsorbing media in enclosures will always reduce the level of gaseous pollutants. Their effectiveness, how-

ever, depends on the type of adsorber used and on the way they are installed[12,13]. Installation of adsorbing material has, of course, also a cost.

Damage to an object from acid deposition depends on the quantity of acid present. A higher steady state concentration will always give a higher net deposition rate to an unsaturated object surface, but any deposition will reduce the concentration of organic acid gas in the enclosure. Thus, even if high concentration of organic acid signifies a high risk of damage to a sensitive object that is to placed in that environment, it does not by itself inform about the risk to any objects already present. The actual risk can be found experimentally by measuring the gas concentration with and without the object present or by modelling the gas deposition and reaction with the object.

To determine the concentration levels of organic acids inside enclosures, it is essential to make measurements[14,15]. Measurements have been performed in different kinds of enclosures, with different geometries and ventilation rates, with and without adsorbing media installed[16,17]. Additional understanding of how acid concentrations depend on enclosure properties can be obtained from modelling. Based on the measured concentration of acid(s) inside the enclosure, the enclosure geometry and the ventilation rate, a model can simulate how the concentration inside the enclosure changes with a change in geometry and/or ventilation rate, or with the installation of an adsorbing medium. Such modelling gives a better understanding of the processes that determine pollutant levels inside enclosures. It can also give useful information about the expected effect of mitigation measures such as the inclusion of adsorbing media[3,16,18].

Most of the physical and chemical parameters of the enclosure such as the geometry, ventilation rate and concentration of the gas(es) are relatively easy to measure on site in the museum. Two parameters that are essential for modelling are the emission and deposition rates of organic acid(s) or other pollutant gas inside the enclosure. The main point in this paper is to add to the measured data available in the literature for the deposition velocity of acetic acid to, and emission rates of some very volatile organic acids, aldehydes and ketones from, heritage materials. Such data are essential for the assessment of the relative sizes of sources and sinks for pollutant gases inside showcases and ultimately for risk assessment based on further information about reaction rates and mechanisms[11]. We also report measured data for the chemical composition of a deposited organic film on the inside of a showcase.

These two parameters, the emission and deposition rates, play an essential role in determining the acid concentration inside the enclosure. The higher the emission rate is compared to the deposition rate, the higher the concentration will be in the enclosure and the slower will be the decrease in concentration with increased ventilation. If either the emission rate or the deposition rate is known, the value for the other can usually be calculated. Measured emission rates from many different materials have been reported[2,19,20,21,22]. It is, however, questionable how well such values represent emissions from construction materials used for museum enclosures. Surface removal rates (K_s) of acetic acid to the insides of six showcases at the British

Museum constructed between 1995 and 1999 were reported to be in the range between 0.10 and 0.15 day^{-1},[18] corresponding to deposition velocities (v_d) in the range between 1.9•10^{-7} and 2.9•10^{-7} ms^{-1}. In previous studies, the deposition velocity of acetic and formic acid (calculated as a single component) to the inside of enclosures was assumed to be similar to values of nitrogen dioxide (NO_2) and ozone (O_3), in the range from 1.6•10^{-5} to 8.9•10^{-5} ms^{-1} and ~ 0 to glass[3,18,23]. Fatty acids with more than 14 carbon atoms, palmitates and stearates, were found on the inside of painting glass[23]. Similar surface deposition velocities were found for NO_2, O_3 and sulphur dioxide (SO_2) to activated carbon adsorbers. The observed increase from 1.4•10^{-3} ms^{-1} at 0% relative humidity to 1.8•10^{-3} ms^{-1} at 90% relative humidity suggests additional dissolution in adsorbed water at increasing humidity[24].

2 Experimental

2.1 Samples

Experiments were performed on three canvas samples obtained from the Tate Gallery in London. The details of the three canvas samples and activated carbon cloth are described in Table 1. Figure 1 shows the larger sheets of the canvases before cutting off the smaller experimental samples. Measured pH values are shown in the photograph at the location where the samples were cut off.

Sample no. Short name	Description
A. New white cotton canvas	12 ounce cotton duck (off white colour). Weight 393 gm^{-2}. 20 warp and 15 weft yarns per cm. Unsized. Loom state purchased from Cornelissens in London, January 2011.
B. New gray linen canvas	Fine portrait linen, washed, stretched and sized by the conservator at Tate (light gray/green colour). Weight: 222 gm^{-2}. 22 warp and 23 weft yarns per cm. Coated with a thin animal glue size, brushed in a warm 5% solution in water saturated with calcium carbonate to make the canvas "conservation grade" with a pH of ~ 6, and applied to one side. 10 g size per m^2 was used. The size coats the yarns and protects them from the oil ground applied on top.
C. Aged brown and degraded canvas	An original un-primed loose-lining from a late Turner (~1846). A loose-lining is a canvas applied by the colourman to protect the back of the main artists' canvas. The original main canvas was primed, but in this case the loose-lining was not. Because it is un-primed the canvas will have been exposed to some external pollution, particulates, sulphur dioxide, hydrogen sulphide and others, from the reverse. The polluted side is darker; the area covered by the stretcher is lighter. The side facing the main original canvas is lighter and less polluted. Probably most of the historical sulphate pollution is on the darker side, but some may have penetrated. According to the conservator at Tate the canvas ought to have been sized with animal glue by the original colourman, but probably this was omitted to save time. Embrittlement and dirt is evident on the canvas. Weight: 250 gm^{-2}. 18 warp and 15 weft yarns per cm. The loose lining was removed from the original in 1960 and has been kept in a wooden drawer since then.
D. Activated carbon cloth, woven.	10 years old. Previously unused. Stored in a closed plastic zipper bag in the laboratory.

Table 1: Description of the canvas samples used for the experiments.

a) pH=6.7

b) pH=8.3
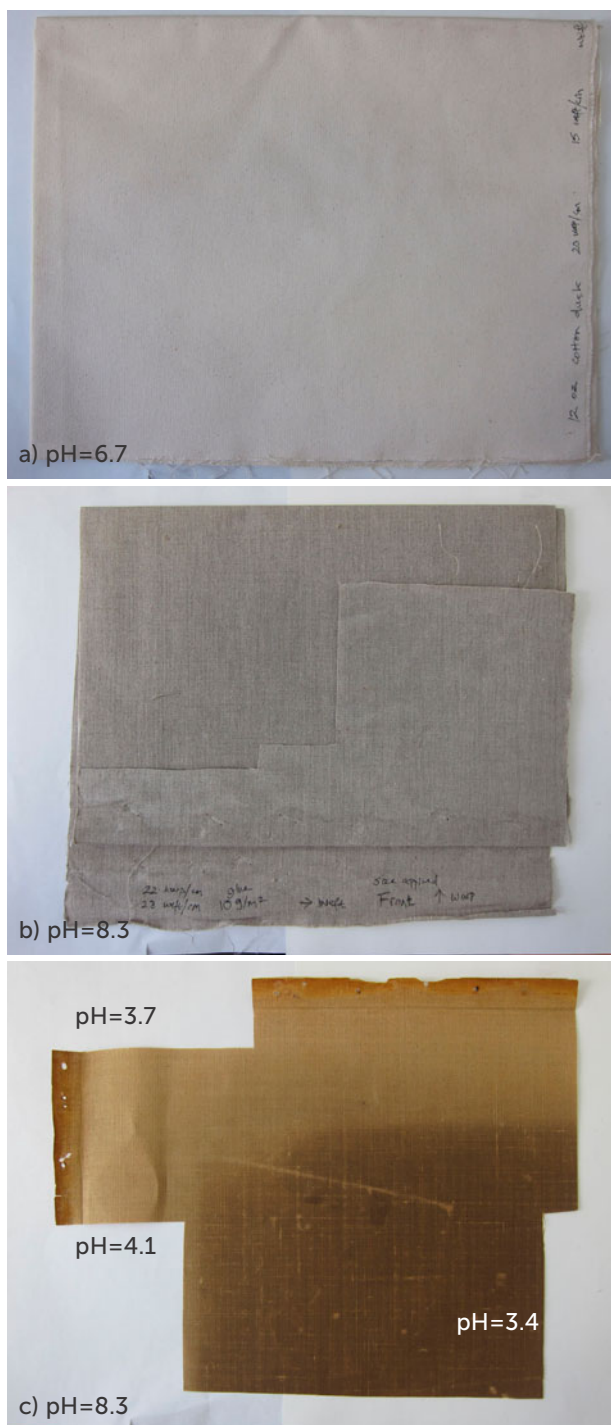

pH=3.7

pH=4.1

pH=3.4

c) pH=8.3

Figure 1: The "Tate canvases" used for the experiments. Measured pH values are shown in the photograph at the location where the samples were cut off.

2.2   Measurement of pH

The acidity of the canvases was measured by cutting 0.5 g of each sample piece in smaller pieces, then wetting and soaking the pieces in 10 ml distilled water (pH 5.5) for 16 h before measuring the pH in the soaking water with a standard glass electrode. One sample was measured for each of the uniform canvases A and B. Samples from three different locations were measured for canvas C (Figure 1), which differed in appearance from the edge to the inner part. The three locations were at the outer edge where the canvas had been tacked to the stretcher, inside this outer edge, where

the canvas had been in front of the chamfered stretcher member, and from the inner soiled area. The inner part which had been exposed to the room atmosphere and wall showed considerable colour change and evidence of soiling, whereas this colour change was less evident on the non-exposed area on the edges and reverse side. The original colour of the canvas would have been similar to sample B.

2.3   Measurement of carbonyl and carboxylic acid emission rates and acetic acid deposition velocities

A canvas sample with an area of 60 cm^2 was mounted free hanging in a Teflon® PFA enclosure (Savillex, Minnetonka, MN, USA) with a volume of 1000 cm^3. The enclosure was temperature-stabilized to 20 °C in a water bath and flushed with humidity-controlled (RH=45%) VOC-free air. Laboratory air was compressed, humidified and sent through a gas cooler (M&C TechGroup Germany GmbH, Ratingen, Germany) for establishing a constant relative humidity. A commercial noble metal catalyst module (Parker Hannifin Corp., Haverhill, MA, USA) operated at 350 °C was used for VOC destruction before delivering a flow of 500 cm^{3}min^{-1} to the sample enclosure via a mass flow controller.

For the acetic acid deposition tests, a small amount of acetic acid (in nitrogen) was added to the main flow from a home-built permeation source to generate a constant acetic acid mixing ratio of ~500 μgm^{-3} in the feed flow. Teflon® solenoid valves (M Series, Teqcom Industries Inc., Santa Ana, USA) were used to periodically sample the air from upstream and downstream the sample enclosure.

A PTR-TOF 8000 (Ionicon Analytik GmbH, Innsbruck, Austria) was used for on-line and real-time measurements of acetic acid and other organic trace gases. The measurement principle and the PTR-TOF 8000 instrument itself have been described in great detail elsewhere[25] and thus only the essentials are described here. Sampling air is drawn into a low-pressure reactor where organic molecules react with hydronium (H_3O^+) ions generated in an external glow discharge ion source. A voltage across the reactor, precisely termed drift tube, generates an electric field which prevents hydration of ions. Non-dissociative proton transfer reactions result in the formation of protonated organic analyte molecules that can be subjected to mass spectrometric analysis. Highly mass resolved analysis in the PTR-TOF 8000 instrument identifies the sum formula of the analyte ions. For the measurements described herein, the PTR-TOF 8000 was operated in its routine mode of operation. The drift tube pressure was 2.40 mbar, the drift tube temperature was 60 °C and the drift tube voltage was 550 V. For calibration, VOC-free air was spiked with a certified VOC standard gas (Apel-Riemer Environmental Inc., Broomfield, CO,

Canvas Sample	Formaldehyde	Acetaldehyde	Acetone/ Propanal	Formic Acid	Acetic Acid	Propionic Acid
A	0.010	0.011	0.0029	0.015	0.061	0.0015
B	0.0017	0.0037	0.0011	0.012	0.022	0.00043
C	0.0021	0.00032	0.00063	0.00083	0.0021	0.000066

Table 2: Emission rates of six most abundant volatile aldehydes and organic acids (μgm^{-2}s^{-1}).

USA). The VOC standard gas contained 5 ppmv of formaldehyde and 1 ppmv of acetaldehyde and acetone, respectively. For the carboxylic acids, we used theoretically calculated instrumental response factors[26]. The accuracy of the carboxylic acid data is ± 20%; the accuracy of the carbonyl data is ± 10%. For data analysis, the "PTR-TOF Data Analyzer" software was used[27].

The emission rates of the carbonyls and carboxylic acids (Table 2) were calculated from equation (1):

$$E=Q \cdot C/A \qquad (1)$$

where E is the emission rate (in $gm^{-2}s^{-1}$), Q is the air flow rate through the enclosure ($8.4\ cm^3s^{-1}$), and A is the area of the canvas sample ($0.006\ m^2$). The average linear air flow velocity through the enclosure was $0.093\ cms^{-1}$. This gives a Reynolds number of 6.6 which signifies laminar flow[28].

The deposition velocity, v_d, of acetic acid was calculated as follows[29]:

$$v_d=(C_0-C) \cdot Q/\bar{C} \cdot A,\ \text{where}\ \bar{C}=(C_0+C)/2 \qquad (2)$$

where v_d is the deposition velocity of the gas to the canvas (in ms^{-1}), and C_0, C and $\bar{C}$ are the trace gas concentrations in the in- and outflow and the average concentration in the enclosure, respectively.

2.4 Measurement of acetic acid deposition to glass

An experiment was conducted to study the adsorption of acetic acid to clean laboratory glass. The acetic acid concentration was measured for four to seven days with passive samplers of the badge type[30,31] exposed inside a desiccator together with an acetic acid source, and after the source was removed and the desiccator inside was cleaned. The acetic acid source, 150 mg sodium chloride (NaCl, analytic grade) soaked with 30 ml acetic acid (100%, analytic grade) and the badge samplers were placed in the 28 l volume glass desiccator for four weeks at RH = 75% and an average temperature of 23-24°C. The acetic acid source was then removed, the glass vessel was thoroughly dry cleaned with normal new hand drying paper before new badge samplers were introduced and it was closed again.

Figure 2: Enclosure with glass front holding wooden and metal objects at the Viking ship museum in Oslo. The whitish appearance of the glass is partly due to the organic film.

Finally, the desiccator was again opened and cleaned with ethanol before introducing new badge samplers and closing. The last cleaning operation with ethanol and sampler measurement was repeated once.

2.5 Measurement of the composition of an organic film adsorbed onto a glass enclosure in a museum

A gas-chromatographic analysis was performed to investigate the chemical composition of an organic film deposited over several years on the inside of a glass enclosure holding wooden and metal objects at the Viking ship museum in Oslo, Norway (Figure 2). The film was collected on a clean quartz filter by wiping the window pane inside gently with the filter. Thermal desorption GC-MS analysis was used to quantify the relative content of the 30 most abundant organic compounds, with less than 15 carbon atoms and boiling points between 60 and 250 °C.

3 Results

3.1 Emissions of carbonyls and carboxylic acids from canvas

PTR-ToF-MS measurements revealed that formaldehyde, acetaldehyde and acetone (or its isomer propanal) and small carboxylic acids including formic acid, acetic acid and propionic acid are the dominant volatile organic species in the headspace of canvas samples (Figure 3). Table 2 summarizes the derived emission rates of the six most volatile aldehydes and organic acids.
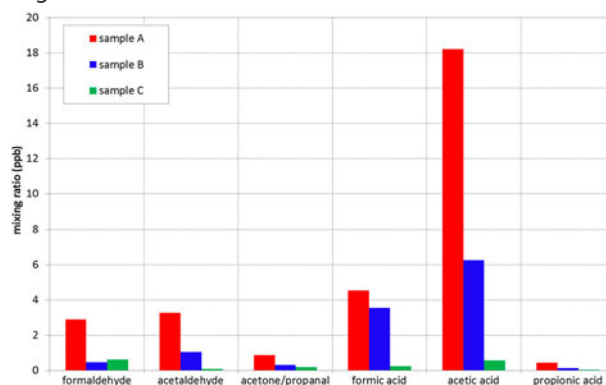

Figure 3: Carbonyl and carboxylic acid concentrations measured in the dynamic headspace of samples A, B and C.

3.2 Acetic acid deposition to canvas

Figure 4 shows the time profile of acetic acid in the enclosure in- and outflow, respectively, when sample A was studied. Acetic acid exposure started at 0 hours and after approximately 42 hours a steady state acetic acid concentration of 474 μgm^{-3} was reached in the enclosure outflow (Figure 4, red curve). The enclosure inflow concentration (Figure 4, blue curve) was periodically monitored over the course of the experiment and it showed only minor variations. The data gaps were caused by instrument and, or software failures. Similar experiments were performed for samples A through D to obtain the acetic acid concentration in the enclosure in- and outflow at steady-state conditions. Table 3 summarizes the measurement results.
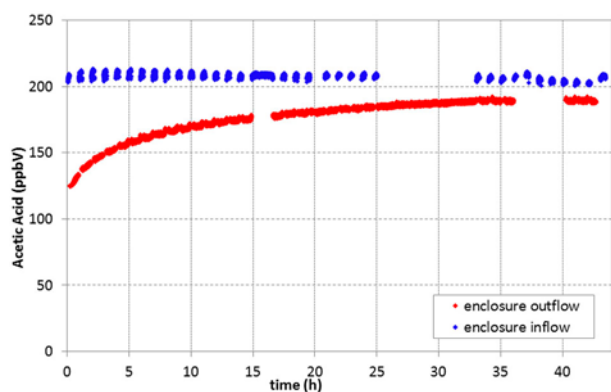
Figure 4: Time-profile of acetic acid in the sample enclosure in- and outflow when sample A was studied.

3.3 Acetic acid deposition to glass

The results from acetic acid measurements in a glass desiccator are shown in Table 4. Initially, an acetic acid source was installed and an acetic acid concentration of 50 ± 7 mg m^{-3} was measured. After removing the source and dry cleaning the surface with paper, the acetic acid concentration still reached a concentration of 33 ± 9 mg m^{-3} confirming that acetic acid efficiently adsorbs and sticks to establish a layer on a glass surface. Only after the surface had been cleaned twice with ethanol, acetic acid levels reached background levels of 0.001 mg m^{-3}

3.4 Composition of an organic film adsorbed onto a glass enclosure in a museum

Table 5 shows the results for the 30 most abundant VOCs with C < 14 found from a GC-MS analysis of the film deposited on the inside window panel of a showcase at the Viking ship museum in Oslo, Norway. A series of carboxylic acids were detected including formic and acetic acid which are known to degrade many materials.

4 Discussion

Acetic acid was the predominantly emitted compound from all three samples and sample A showed the highest emissions of all samples, followed by sample B and C. This may be explained by the large surface area of untreated cotton (A). Acetic acid emissions from sample B were 10 times higher than from sample C even if the latter was more acidic than the alkaline sample B. Acetic acid in the old and soiled sample C may be more fixed to the cloth than in the newer sample B. The second most abundantly emitted compound was formic acid, followed by acetaldehyde and formaldehyde. Formaldehyde from the old sample C were as high as from sample B.

Measured deposition velocities to the canvas samples ranged from $8.9 \cdot 10^{-6}$ ms^{-1} to $9.5 \cdot 10^{-5}$ ms^{-1}. It is noted that the linear air flow velocity along the sample surface (~ 0.001 ms^{-1}) was significantly higher than the measured deposition velocities. The transport resistance in air would thus be close to zero with the measured deposition velocities corresponding to the surface deposition velocities.

Sample	pH	Inflow concentration (μgm^{-3})	Outflow concentration (μgm^{-3})	Sampling time (h)	Deposition velocity (ms^{-1})
A	6.4	518.0	475.0	42.5	$9.5 \cdot 10^{-5}$
B	8.3	505.5	491.5	88	$3.9 \cdot 10^{-5}$
C	3.7*	503.8	500.5	42	$8.9 \cdot 10^{-5}$
D	n.a.	489	198.5	9	$6.8 \cdot 10^{-5}$

Table 3: The pH value measured in soaking water, the acetic acid concentrations measured in the sample enclosure in- and outflow at steady state conditions, the sampling time (i.e. the time when steady state was reached) and the derived acetic acid deposition velocities.

	With acetic acid source	Without acetic acid source Dry cleaned with paper	Without acetic acid source Cleaned with ethanol	Without acetic acid source Cleaned twice with ethanol
Concentration (mg m^{-3})	50±7 (2)	33±9 (4)	0.2 (1)	0.001 (1)

Table 4: Acetic acid concentration in a glass desiccator under various conditions. The uncertainty is the standard deviation of the replicate measurements. The number of replicates is reported in brackets.

Compound	Concentration (toluene-equivalents) (ng per cm^2 of filter.)
Benzenecarboxylic acid	2087
Formic acid	797
Acetic acid	768
Cyclopropyl carbinol	657
Phenol, 2-methoxy-	565
Hexanoic acid	541
Nonanoic acid	486
2-Propanone, 1-hydroxy-	395
Octanoic Acid	370
Acetone	336
Methyl vinyl ketone	191
1-Hexadecene	318
2-Furanmethanol	120
Pentanoic acid	104
1-Hexene, 5,5-dimethyl-	103
Butyrolactone	60
Toluene	57
2-Furanmethanol, tetrahydro-, acetate	48
Triethylene glycol	44
2-Pyrrolidinone, 1-methyl-	40
Bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde, 6,6-dimethyl- (Myrtenal)	40
Phenol	34
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	25
Carbon disulfide	21
1-Pentanol, 2,2,4-trimethyl-	15
Benzene, 1-methyl-3-(1-methylethyl)-	14
2,4-Dimethyl-2-oxazoline-4-methanol	12
Diethyl Phthalate	10
2,5-Hexanedione	4

Table 5: Organic compounds deposited on the inside window panel of a showcase at the Viking ship museum in Oslo, Norway.

The lowest deposition velocity was measured for the oldest and most acidic sample (C). It is likely that the acidic surface of this sample reduced the deposition velocity. Even at pH 3.7, acetic acid is essentially undissociated and will therefore not be involved in the hydrolysis of cellulose. The deposition velocity did not correlate with pH for the three samples. Other factors such as surface porosity and roughness of the textiles are likely to have a larger influence on deposition velocity. The untreated cotton canvas (A) has a larger exposed surface area than the glue-sized linen (B).

Deposition velocities for acetic acid measured in showcases at the British Museum[17] were 1 to 2 orders of magnitude (31-500 times) lower than the values obtained here. While the showcases at the British Museum contained smooth aluminium foil surfaces, the woven textiles used here have a more open structure offering a larger and possibly more humid surface area for adsorption. In addition, still air inside the showcases may have increased increased the resistance for the transport to the surface. The deposition velocities of acetic acid measured to the canvases ($8.9 \cdot 10^{-6}$ to $9.5 \cdot 10^{-5}$ ms^{-1}) are similar to those found for inorganic gases infiltrated into showcases ($1.6 \cdot 10^{-5}$ to $8.9 \cdot 10^{-5}$ ms^{-1})[3]. The observed deposition velocity of acetic acid to an activated carbon cloth ($6.8 \cdot 10^{-4}$ ms^{-1}) was, however, a factor of two smaller than previously measured for inorganic gases (1.6-$1.7 \cdot 10^{-3}$ ms^{-1})[24].

It seems that the deposition velocity of acetic acid to the inside surfaces of showcases will typically not reach the maximum values of an absolute absorber. It can cover a wide range from $1 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$ ms^{-1} depending upon the types of surfaces and air flow conditions inside the showcase. Lower values are more likely associated with smooth, hard and non-reacting surfaces and low ventilation conditions when the air in the enclosure is still. Rougher, potentially alkaline surfaces and higher ventilation and thus more efficient mixing will result in higher values.

The simple experiment with the acetic acid source in the glass desiccator confirmed that acetic acid efficiently adsorbs and sticks to establish a layer on a clean glass surface.

The film deposited on the inside window panel of a showcase at the Viking ship museum in Oslo contained a series of carboxylic acids. Amongst these, we also found formic and acetic acid which are known to degrade many materials. It is reasonable to assume that the acidic film is distributed over all surfaces inside the showcase increasing the risk of corrosion and surface degradation of the exposed objects. The degree of corrosion and surface degradation will depend upon the object type, the composition of the film and the climatic conditions. Another negative side effect is that such a surface film on the window panel may be visually disturbing. It is recommendable to prevent the build-up of such acidic films by appropriate measures (physical removal, installation of adsorbing materials, increased ventilation).

5   Conclusion

Acetic acid (and other organic acids) may be abundantly present in showcases used for protecting cultural heritage objects. It is well known that object surfaces can be degraded by deposited acids. Object surfaces may sometimes be protected with surface coatings, but in most cases it is mandatory to reduce acid concentrations. The main factors determining the concentration of acetic acid inside an enclosure is the acetic acid emission rate from the object itself and the inside surfaces of the enclosure, the acetic acid deposition rate to all surfaces inside the enclosure and the ventilation rate of the enclosure. Lowest acid concentrations can be achieved if emissions are kept low and if deposition rates and ventilation rates are high. Increased ventilation rates may, however, lead to increased infiltration of external air pollutants such as ozone or nitrogen dioxide. Acetic acid was found to effectively deposit to activated carbon cloths which may be used to scavenge the pollutant from the air inside the enclosure. Installing and periodically exchanging activated carbon cloths (or other adsorbent media) inside a museum enclosure appears to be an efficient way to reduce volatile organic acid concentrations in the enclosure.

6   Acknowledgements

7   References

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