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RESPONSE OF LEAD DEPOSITED ON GLASS TO ACETIC ACID EXPOSURE, WITH POTENTIAL FOR ITS APPLICATION AS AN ACETIC ACID DOSIMETER/SENSOR.

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Abstract

Small glass substrates were coated with a thin granular lead film by thermal vapour deposition in order to test the feasibility of using lead-coated glass as sensors for detecting the presence of gaseous acetic acid in air. The lead-glass samples were exposed to acetic acid in increasing concentrations, at a controlled temperature of 23ºC and 54% relative humidity for a period of 60 days. The change in the lead films on exposure was systematically investigated by measuring the variation in light transmission at a wavelength of 379 nm. Initial corrosion of the deposited reactive thin lead films leading to lead oxide and lead hydroxycarbonates and/or lead carbonates probably occurred. The analysis showed that the main response was due to corrosion of the lead film and granules with conversion to lead hydroxyl-carbonates and/or carbonates and formation of lead acetate. In addition, about 30% of the response was found to be due to acetic acid adsorption on the lead-glass samples. After about 15 days exposure significant saturation and decrease in sensitivity was observed.

1 Introduction

The measurement of formic and acetic acid in indoor cultural heritage environments and assessment of damage risk to cultural heritage objects is of great importance[1,2]. Organic acids have been shown to damage heritage objects made from lead, copper, calcareous materials, varnish, pigments, sensitive paper and other materials[3-6]. The concentration of the organic acids in air can be measured with passive samplers[7-9]. These are relatively inexpensive, accessible and well suited for use in cultural heritage environments. Alternatively, the impact of organic acids on sensitive dosimeter materials can be measured, and the effect compared with the sensitivity of heritage objects[3,10]. Materials that are particularly sensitive to formic and acetic acid, such as special glass compositions and lead, can be used as dosimeters[1,2,8,11,12]. Here we present a new technique for the production of lead dosimeters and measurement of the lead corrosion for this application. Thin granular lead films were deposited onto a glass surface by thermal metal vapour deposition. The films were exposed to acetic acid vapour in controlled environments and the corrosion effect was measured by UV/visible light spectrophotometry. The expected corrosion of the fresh lead surfaces occurs rapidly in air according to[13]:

$$2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2 \qquad (1)$$

$$Pb + O_2 \rightarrow 2PbO \qquad (2)$$

The presence of other anions, e.g. from air pollution, will further react with the oxidized surface. The presence of acetate is expected to lead to lead acetate corrosion according to:

$$Pb(OH)_2 + 2CH_3COOH \rightarrow Pb(CH_3COO)_2 + 2H_2O \qquad (3)$$

Here we have investigated if the method of spectrophotometric detection of acetic acid corrosion of lead films on glass could potentially be implement-

ed for dosimeter or sensor applications. In the following, the more general term sensor will be used, but keeping in mind that the investigated method is based on the principle of recording with time the cumulative impact of a dose of the environmental influences. This could potentially be interpreted as the parametric presence of, for example, the concentration of acetic acid.

2 Methods

Thin granular lead films were produced by thermal metal vapour deposition on one side of the (1.5x0.7x0.1 cm) glass pieces. The deposition was performed at room temperature in a thermal evaporator with $7x10^{-6}$ mbar base pressure and ~15 s deposition time. Before the deposition, the glass substrates were degreased with trichloroethylene and cleaned with acetone and isopropylalcohol (IPA) in ultrasonic bath, and blown dry with N_2 gas. A granular film of (12 ± 2) nm average thickness was deposited, shown in Figure 1, with a 1.53 nm RMS (Root Mean Square) roughness without the granules. For depositions at room temperature, granulation is expected to occur on insulating substrates[14, 15]. The glass was transparent after exposure and could not be distinguished from non-lead covered glasses by the naked eye. Four different glass samples coated with the lead film were mounted in special holders adapted for the UV/visible light spectrophotometer measurements (Agilent 8453). Two glass samples were mounted as duplicates in one of three sample holders. The three holders containing the samples were exposed to different constant concentrations of acetic acid in three individual glass vessels of 27 L volume at relative humidity (RH) of 54% and temperature of 23°C for 60 days (see Figure 2). In addition to the exposures of the lead films, blank exposures were performed under the same conditions. The blanks consisted of three sample holders mounted with four clean glass pieces without lead coatings. The absorbance response by the spectrophotometer is the measure of the transmitted light compared to the incident light on the specimen under study. This provides information on the lead based sensor properties, including the impact of acetic acid.

The constant RH and average acetic acid atmosphere was produced by mixing glacial acetic acid (100%) into saturated aqueous solutions of $MgNO_3 \cdot 6H2O$ in small beakers, according to Tétreault et al.[16] and Brokerhof and Bommel[17]. They report quite different empirically observed monthly average concentrations of acetic acid for their experimental conditions. Tétreault et al. report a concentration of:

$CH_3COOH(g) = 37:8 \times CH_3COOH(aq)$
(0.06 to 36 %v/v)   (4)

while Brokerhof and Bommel[17] report a concentration of:

$CH_3COOH(g) = 2.5 \times 10^{(1.776+(0.806*LOG(CH3COOH(aq))}$
(0.05 to 25 %v/v)   (5)

where $CH_3COOH(g)$ (mg/m^3) is the acetic acid concentration in the vapour phase, and $CH_3COOH(aq)$ (%v/v) is the acetic acid concentration in the aqueous phase. Concentrations of acetic acid calculated from Eq. (5) are about seven times higher at 0.05 %v/v acetic acid

(13 vs 2 mg/m^3),changing to about two times higher at 25 %v/v (2000 vs 950 mg/m^3).

Tétreault et al.[16] report use of less acetic acid solution (3 ml in 15 g $MgNO_3 \cdot 6H_2O$) in smaller jars (400 ml) than Brokerhof and Bommel[17] (12.5 ml in 50 g $MgNO_3 \cdot 6H_2O$ in jars of 1000 ml). Tétreault et al.[16] observed a reduction in the concentration with 23% over the monthly
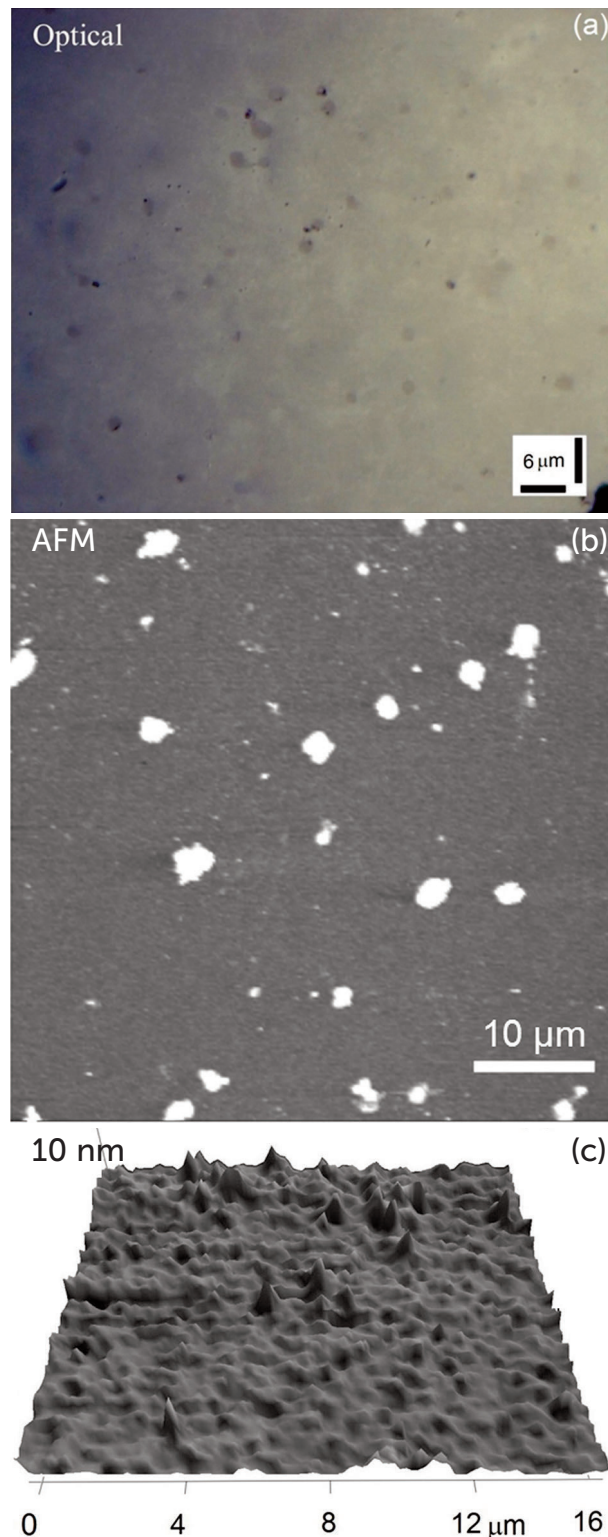

Figure 1: Optical microscopy (a) and atomic force microscopy (AFM) (b) images of the fresh vapour deposited lead film on glass substrate show the dimension and distribution of granules. Atomic force microscopy image of the lead film without granules (c).

period due to a certain air exchange of the glass jar and absorption/desorption reactions on exposed experimental lead samples. Brokerhof and Bommel[17] did not observe a reduction in air-concentration during one month. In this work the samples were exposed to 10 ml acetic acid solution in 50mg $MgNO_3 \cdot 6H_2O$, in considerably larger glass vessels of 27 litres. The glass vessels were opened (quickly) every third day, on average, to do measurements of the sample response, which gave some undetermined air exchange. The adsorption/absorption on the very small samples would insignificantly influence the acetic acid air concentration. The possible influence of the larger internal volumes and surfaces of the glass vessels is unknown. It was beyond the resources of this work to perform measurements of the acetic acid concentration in air. Due to the differences in concentrations reported in

No of samples	Total exposure time (days)	Acetic acid (CH_3COOH) experimental concentration: in solution (%v/v); (indicative range for the concentration in air calculated from the literature (mg/m^3))	
		Until 7 days	From 7 until 60 days
1	60	Low: 0.003% (0.1-1.4 mg/m^3)	0.06% (2-15 mg/m^3), new
2	60	Medium: 0.03% (1-9 mg/m^3)	0.03% (1-9 mg/m^3), new
1	60	High: 0.3% (11-57 mg/m^3)	0.3% (11-57 mg/m^3)

Table 1: Lead films and exposure conditions. The liquid concentration is given by volume (%v/v). The range for the possible concentration in air (mg/m^3) is indicated in brackets in each case, as given from calculations according to Tétreault et al.[16] and then Brokerhof and Bommel[17]. "new" denotes that a new fresh acetic acid solution was installed from 7 days.
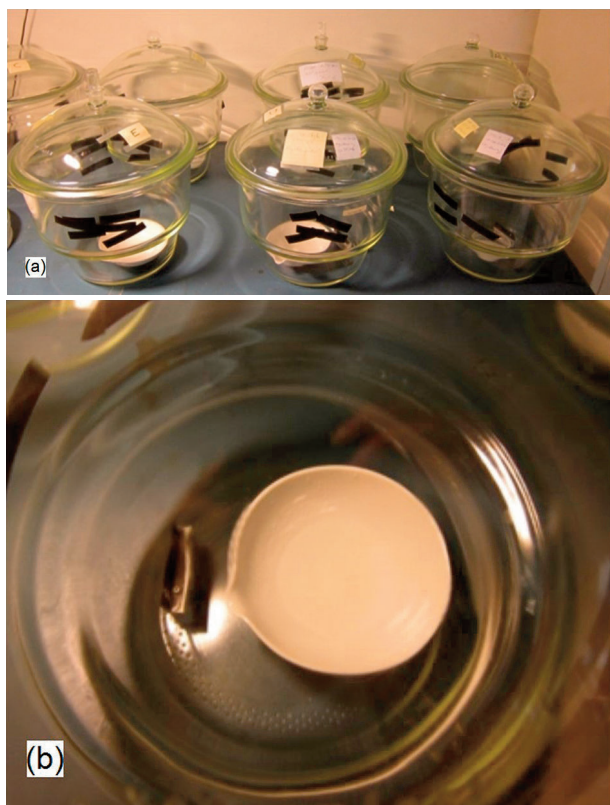

Figure 2: Exposure of granular lead films on glass substrates inside three glass vessels at RH = 54% with different acetic acid concentration (a). Glass sample holder and beaker with the saturated salt and acetic acid solution (b).

the literature for relatively similar exposure experiments, here we report based on the liquid solution concentration values (%v/v), and then the air concentrations as low, medium and high, together with the only indicative range of values calculated from Tétreault et al.[16] and Brokerhof and Bommel[17], by Eqs. (4-5).

Beakers with acetic acid solutions of known concentrations (Table 1) were put into closed glass vessels. The holders with samples were placed in the bottom of the glass vessels beside the beakers (see Figure 2). The samples were removed at approximately regular intervals to be measured in the spectrophotometer. They were measured within the spectral range where the change in absorbance due to the exposure was observed to be at its maximum, more specifically around the broad peak at 379 nm wavelength (see vertical dashed red line in Figure 3). Each spectrophotometer measurement lasted approximately 15 min, with the glass vessels kept closed during the measurement. Although some acetic acid vapour would escape when opening the glass vessel, it would be replenished from solution and from adsorbed acid on the glass inside[18]. As for the exposures reported by Tétreault et al.[16] some reduction in the concentration may have happened over the exposure time. The acetic acid-salt saturated solutions used for the initial exposure of the lead films were already inside the glass vessels from a previous exposure. However, due to an undetectable change in the absorbance response of the films initially exposed to 0.003% and 0.03% acetic acid solutions, by volume (v/v), these solutions were replaced after seven days to assure no depletion. The solution with 0.003% acetic acid was replaced with a solution of 0.06% concentration, whereas the solution with 0.03% acetic acid was changed to a fresh solution of the same concentration, as detailed in Table 1.

For comparison with Table 1, the concentration of acetic in room air in museums and cultural heritage buildings have been measured to usually be below 0.1 mg/m^3, but up to a few hundred μg/m^3 [18,19,20] and occasionally higher in locations with high emitting materials[21]. Higher concentrations, up to a few mg/m^3, have been measured inside protective enclosures[22, 23].

Optical microscopy (Leitz Orthoplan), atomic-force microscopy (AFM - Asylum Research MFP-3D) and scanning electron microscopy with elemental analysis (SEM-EDAX, JEOL SEM 6480 LV-Oxford INCA X-Act SDD X-ray detector, standardless mode (Semi-quantitative), energy optimization done at 5kV) were used to characterise the structure of the fresh vapour deposited granular lead films. After exposure to acetic acid for 56 days the vapour deposited lead film samples were again investigated with the optical microscope, and with AFM and SEM-EDAX instruments after 9.5 months storage in the laboratory, wrapped in Al-foil at T = 23°C and RH < 40%.

3   Results and discussion

Figure 3 shows the spectra for the light absorbance of the samples with vapour deposited lead films before and after 56 days exposure with 0.03% and 0.3% acetic acid. An overall increase in absorbance over the whole spectrum was observed, rather than peaks, which would indicate specific chemical absorption. This

behaviour indicated the expected acetic acid corrosion of the lead thin film to lead oxide and/or lead acetate, and a proportional reduction of the light transmission through the films by increased absorption, and possible reflection and/or scattering. In the following, the spectrophotometer measured values will be noted as absorption values in accordance with the instrument readings.

A clear correlation was observed between the concentration of acetic acid and the increase in light absorbance at 379 nm in the vapour deposited lead films. When comparing the change in absorbance for the vapour deposited lead-glass films (Figure 4a), to the change in absorbance for the bare glass substrates
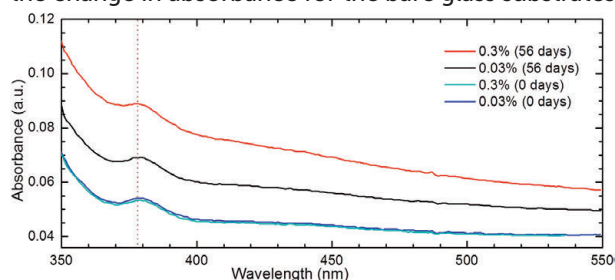

Figure 3: Light absorbance spectra of vapour deposited lead films on glass before exposure and after exposure with 0.03% and 0.3% acetic acid for 56 days.
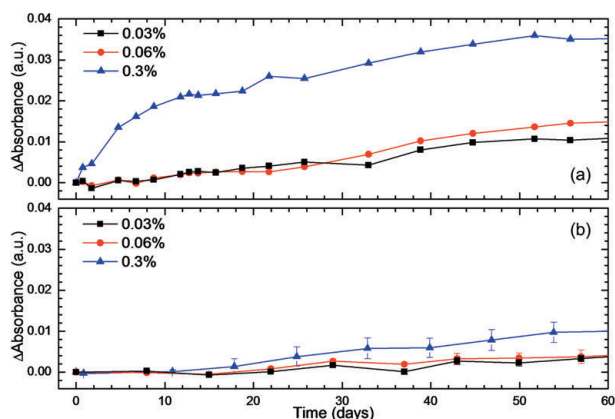

Figure 4: Change in light absorbance at 379 nm for (a) the exposed vapour deposited lead films on glass and (b) the bare glass substrates exposed to solutions of 0.03%, 0.06% and 0.3% acetic acid concentrations.
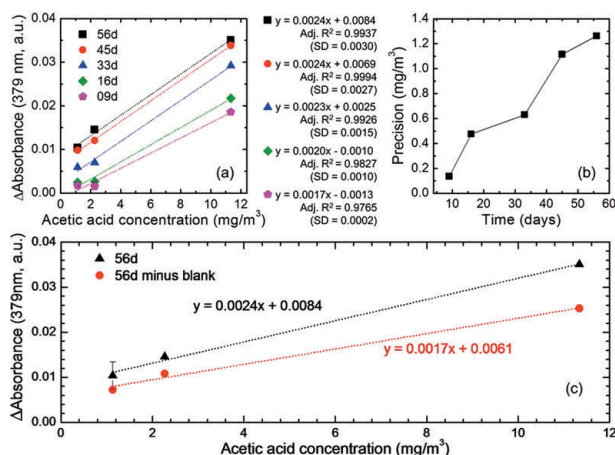

Figure 5: Correlation between the lower estimated values for the concentration of acetic acid (as given from Tétreault et al.[16], see Table 1) and the measured change in light absorbance at 379 nm (a). SD = Standard deviation of duplicates exposed at 0.03%. The calculated duplicate precision (b); and the blank fraction of the final response after 56 days (c).

(Figure 4b) exposed to the same acetic acid concentrations under the same conditions, a significantly higher response was observed for the lead-glass films, indicating its potential as an acetic acid gas sensor.

The correlations between the lower estimated acetic acid concentration in the ranges given in Table 1, and the values measured by the spectrophotometry, recorded as change in light absorbance at 379 nm for the selected days during the 56 days overall exposure time is shown in Figure 5a. A similar figure could be produced for the high estimated acetic acid concentration in the ranges (from Brokerhof and Bommel[17]) given in Table 1. The indicative results reported below for the precision/sensitivity are for the possible range of acetic acid concentrations (Table 1), with exemplification of the derivation given for the low values in the ranges, by Figure 5.

Using the Beer-Lambert law, $A = \varepsilon bC$, where A is the measured absorbance, ε is the wavelength-dependent molar absorptivity coefficient, b is the light path length and C is the measured acetic acid concentration, an indication of the sensor duplicate precision, which could also be interpreted as its respective sensitivity, could be estimated. In Figure 5a the slopes of the graphs then represent the factor εb. By inserting the duplicate standard deviation (SD) for the samples exposed with 0.03% acetic acid for y in the trend equations in Figure 5a (for the low concentration prediction from Tétreault et al.[16]), and disregarding the constants, one obtains concentration values representing the respective sensor duplicate precision/sensitivity over the exposure days, as shown in Figure 5b.

The precision/sensitivity is clearly decreasing with time, until at 56 days of exposure it was indicated to be in the range from 1.25 mg/m^3 as seen in Figure 5b to 6 mg/m^3 (~0.03% v/v), i.e. a similar value as the exposure concentration. For the reporting of a more precise measure of the precision/sensitivity, measured values for the acetic acid concentration in the air in the experimental vessels would have been needed. The increasing uncertainty in the response and decreasing precision/sensitivity shows sensor saturation, which was probably due to passivation of the lead film caused by acetic acid adsorption and/or lead corrosion.

Figure 4a shows the possible effect of the acetic acid adsorption on the absorbance response, strongest for the lead-glass sample exposed with the higher concentration of 0.3%. After about 15 days of exposure the absorbance response shown by the higher concentration curve follows a linear trend similar to the bare glass sample exposed to the same concentration, indicating sensor saturation. In Figure 5c the red curve shows the absorbance response from the lead-glass sample exposed for 56 days, with subtracted absorbance response from the bare glass sample exposed for the same period. This indicates that about 30% of the total loss of transmission after 56 days exposure was purely due to acetic acid adsorption.

Additionally, it was observed by optical microscopy that a substantial translucent and viscose film (Figure 6 and 7) had formed on the lead film-glass surface after exposure to the acetic acid, probably due to adsorption of acetic acid[24]. The light absorbance of bare glass substrates exposed to acetic acid, shown in Figure 4b,
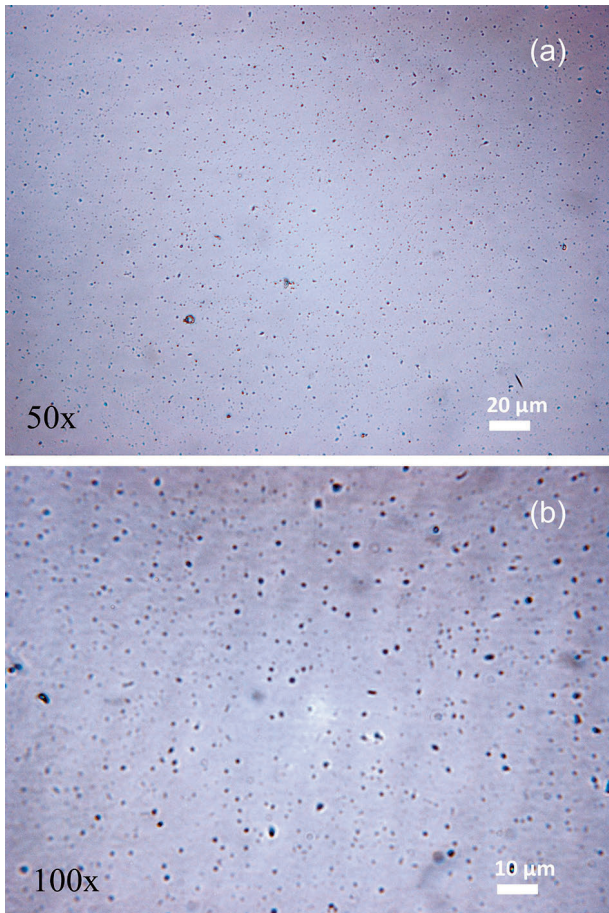
Figure 6: Optical microscopy images with different magnification, of the vapour deposited lead film on glass exposed with a solution of 0.03% acetic acid at RH = 54% for 56 days.
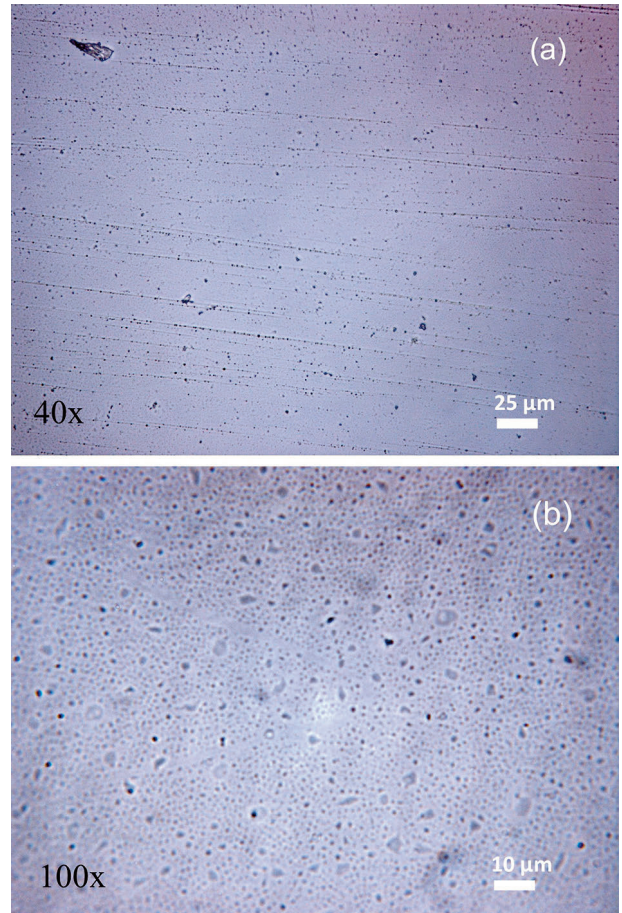

Figure 7: Optical microscopy images with different magnification, of the vapour deposited lead films on glass exposed with a solution of 0.3% acetic acid at RH = 54% for 56 days.

was observed to increase mainly due to the formation of the adsorbed film of acetic acid. Thus, the variation in the values and slopes of the linear fitting shown in Figure 5a, after 16 days of exposure, could be explained by reduced light transmission due to an increasing thickness of an adsorbed acetate film, in addition to the corrosion and formation of lead acetate on the surfaces of the lead and oxidized lead granules.

Figure 8 shows AFM images of the acetic acid exposed lead films, as in the initial optical microscopy images (Figures 6 and 7), but after an extended period of storage. Different granules distributions over the film surfaces and some degree of crystallization can be seen. Table 2 presents the average diameter and thickness of the larger granules observed.

The lead granules on the fresh unexposed lead thin films were wider and thinner than the granules observed on the exposed samples. The concentration of acetic acid vapour adsorbed on the lead film seemed to affect the mechanism for the acetic acid

corrosion of the lead and the pattern of crystal growth. The measurements indicated the formation of granules with a relatively larger diameter after exposure with 0.06% acetic acid compared to the granules formed at exposure with 0.3% acetic acid. The latter showed a denser surface distribution of granule, with several small granules distributed evenly at a distance from and between the larger ones.

Figure 9 shows the SEM images of the lead films exposed to the three acetic acid concentrations after an extended storage period. The grey particles indicate the presence of elements with lower atomic number in addition to lead. Heavy elements, such as lead, have a higher signal/noise ratio (higher electron emission), consequently showing a brighter white. These bright white spots were observed in many of the larger corroded particles indicating the presence of pure lead. A higher density of particles was observed on the sample exposed with the highest concentration of 0.3% acetic acid, as also indicated by the AFM images. A substantial variation in the areal density of corroded particles was observed, especially on this sample.

Due to the very thin lead film (~10 nm) and the small dimensions of the lead granules, the SEM-EDAX elemental analysis proved to be challenging. The EDAX interaction volume included a significant amount of the glass substrate. Thus, in addition to the expected lead and lead corrosion elements such as Pb, O and C, other elements present in the glass (Na, Mg, Al, Si) were also detected. As oxygen is found in both lead corro-

Exposure concentration:	Unexposed (Figure 1) (n = 30)	0.03% (Figure 8) (n = 120)	0.06% (Figure 8) (n = 51)	0.3% (Figure 8) (n = 58)
Average granule diameter (μm)	2.85 ± 0.24	0.96 ± 0.17	1.35 ± 0.23	0.95 ± 0.18
Average granule thickness (nm)	148 ± 37	419± 94	435 ± 78	361 ± 83

Table 2: Sizes, thickness and average absolute deviations for major larger granules observed on lead vapor deposited films on glass. n = number of granules sampled.
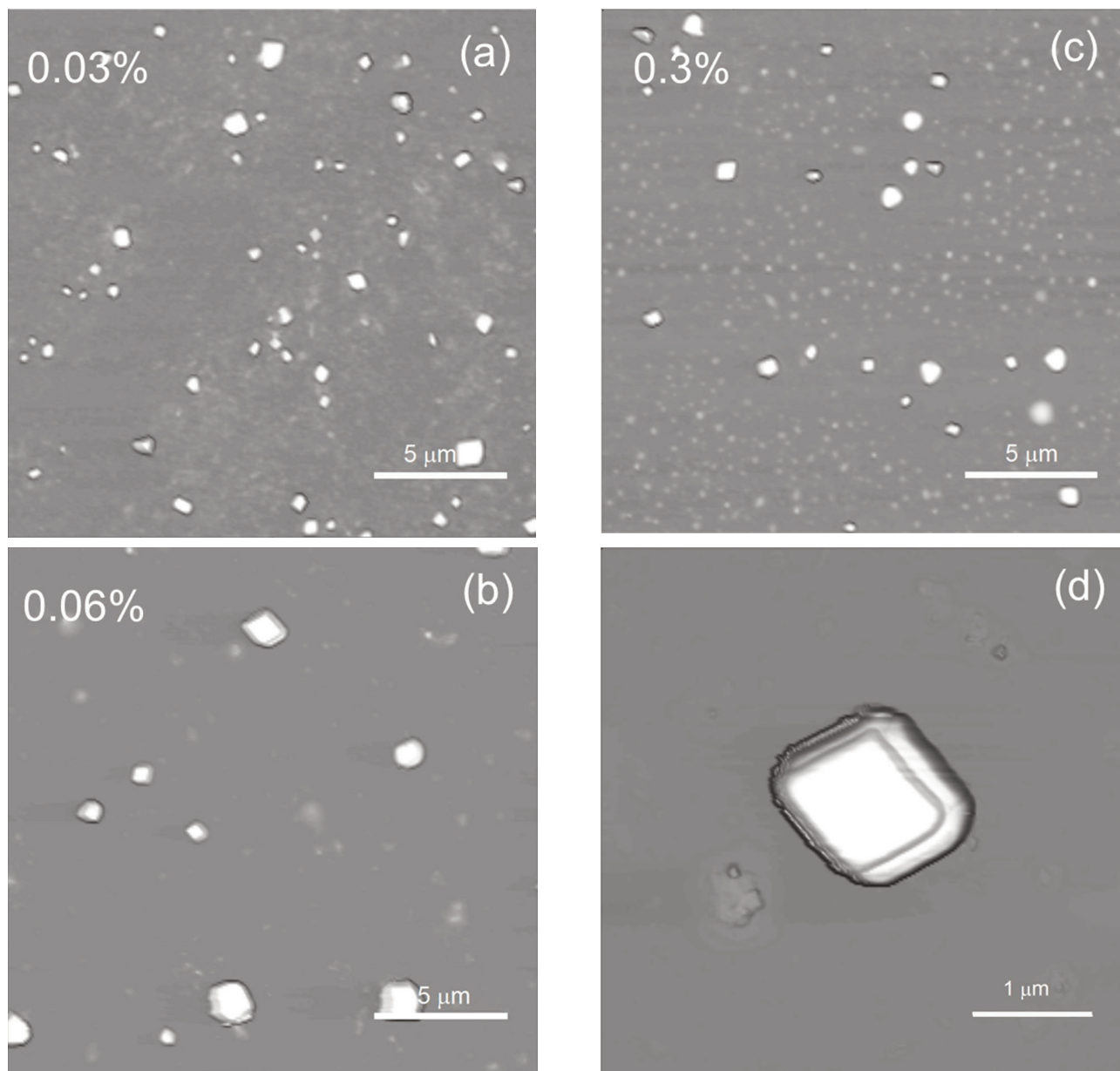
Figure 8: AFM images of the vapour deposited lead films on glass after 56 days of exposure with 0.03% (a), 0.06% (b), and 0.3% (c), acetic acid concentrations (v/v) after an extended storage period. A single granule from (b) with some crystalline structure (d).

sion products and in glass, it was not possible to determine with certainty its proportions to the detected Pb and C in the lead corrosion film. Thus, the measured ratio of oxygen to the other elements could not be used for identifying corrosion products.

However, the detected presence of carbon in the initial thin deposited lead granulate film, with an oxygen to carbon average atomic percentage ratio of $O/C \leq 5.5$, measured at a lower acceleration voltage of 5 kV, possibly indicated the rapid formation of, cerussite ($PbCO_3$, $O/C = 3$) and, or hydrocerussite ($Pb_3(CO_3)_2(OH)_2$, $O/C = 4$).

It has been suggested that humidity modification of acetic acid solutions resulting from the addition of magnesium nitrate hexahydrate would produce nitric acid, which could influence the corrosion[25]. It should be noted that no nitrogen, N, was detected in the films by the SEM-EDAX analysis. It thus seems either no direct nitric acid corrosion have taken place or an extremely small non-detected amount is present in the sample. The artificial atmospheres were clearly dominated by acetic acid, as was readily apparent by the smell. Any protons bonded to hypothetically released nitric acid would anyway originate from the acetic acid, and it seems uncertain if this would affect the acidity on the lead surfaces and corrosion rates.

The reported results are from a few samples and experimental acetic acid exposures. The observed variation in acetic acid detection by corrosion of the lead granulate films on glass, as measured by light spectrophotometry and observed by microscopy, should thus be regarded as indications of the potential applications of this lead-based sensor. More laboratory investigations and experimental exposures are needed to better understand the sensor properties, the corrosion process and products on the vapour deposited lead films on glass, in order to precisely determine the dose-response equation for the sensor. It is essential to understand its sensitivity and saturation point as a
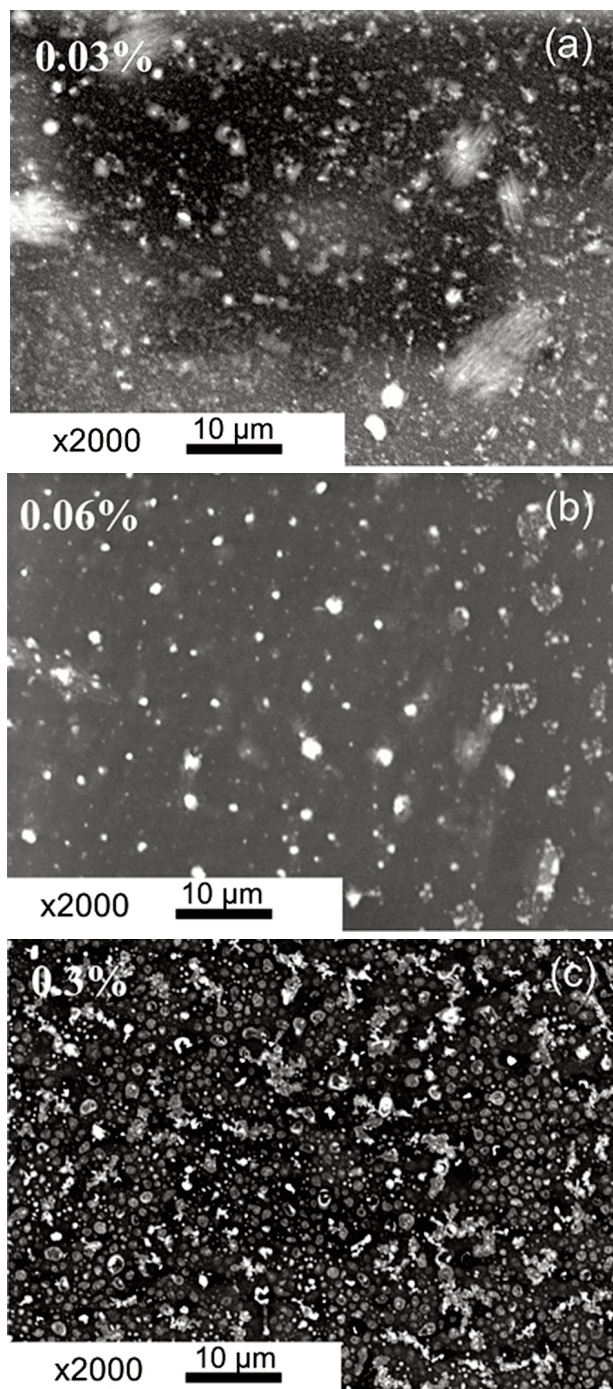
Figure 9: Scanning (secondary) electron microscopy images of the vapour deposited lead films after 56 days exposure with 0.03% (a), 0.06% (b) and 0.3% (c) acetic acid concentration after an extended storage period.

function of film thickness and other characteristics. Lead corrosion is known to be humidity dependent[16,17,26] and further tests are needed to investigate, in particular, the dependence of the sensor response on relative humidity. For possible application of such lead films to measure acetic acid concentrations in indoor ambient air, it would be necessary to perform field tests with exposure in real indoor environments with simultaneous measurement of the organic acid concentrations and other influencing parameters, such as relative humidity and temperature.

Questions, which needs addressing, are if similar acetic acid adsorption will happen in the indoor as was detected in the laboratory experiments, and if the sensor sensitivity would be sufficient. It should be noted that such "impact sensors" do not recover, so they need changing at saturation. This may limit application. The selectivity of the sensor is expected to be similar to other lead thin film corrosion sensors, such as lead coated piezo electric crystals (L-PQCs). Most of the indoor corrosion on L-PQCs has been found to be due to acetic acid impact. In a large field test campaign indoor in 30 museum locations, the explanatory power of the acetic acid impact was found to be 83% (R^2 = 0.83), with no significant correlation found for other environmental parameters (formic acid, TVOC (Total Volatile Organic Compounds), nitrogen dioxide (NO_2), Ozone (O_3) sulfur dioxide (SO_2), humidity, temperature and light)[8]. The lack of observed independent correlation with formic acid in that study may have been due to domination by much higher acetic acid concentrations. This indicates a potential for interpretation of the measured result as the parametric presence of acetic acid, possibly together with formic acid, as an indicative concentration value. The common present way of using such generic impact sensors, or "dosimeters", is however by comparison of results values with object sensitivities in different ways[3,10]. Chemical analysis of corrosion products is possible, but this is not a directly measured sensor response.

Dust impact is a separate important concern, which can however be reduced by the proper mounting of sensors with sheltering during exposures, and by avoiding excessively long exposure times, which could allow soiling by diffusion. In the rare cases when significant dust impact on the sensors is still observed, it is likely that this is a main concern for objects too, besides any possible acid impact.

Experiments with more parallels and samples in the laboratory and field would be needed to assess the reproducibility of measurements.

4   Conclusion

Small glass substrates were coated with a thin lead film, of average thickness of 12 ± 2 nm, by metal vapour deposition. The film contained evenly distributed lead granules approximately 3 µm in diameter and 150 nm thickness with smaller granules in between. The film showed measurable sensitivity to acetic acid concentrations in air from low to high values, probably from a range of 1-10 to a range of 10-60 mg/m^3. A clear correlation was found between the exposure concentration and the response, measured as the change in light absorbance at 379 nm. The main response observed was most likely due to corrosion of the granular lead film, probably mostly to lead acetate but partly also to lead oxide and carbonate. Approximately 30% of the response measured after 56 days was probably due to the formation of a film of adsorbed acetic acid. Lead carbonate was observed on the freshly deposited lead granulate films. After the acetic acid exposure and storage in the laboratory, crystals probably containing lead acetate corrosion products were observed on the samples.

Vapour deposition of sensitive lead films on glass and detection of corrosion by change in light transmis-

sion/absorption has the potential to be developed as a method for sensing of acetic acid in air. Further experiments in the laboratory and indoor field-tests are needed to precisely determine the sensitivity and dose-response correlation for the detection of acetic acid vapour in indoor air by reactive lead vapour deposited films on glass. This would include studies of the impact of the influencing parameters, especially the organic acids, of other pollutant gases that may be present, and of air humidity and temperature.

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