Acid-detector (A-D) strips were originally developed to assess the deterioration of acetate film stock, but they can also be used more generally within enclosures to detect volatile acidic pollution. A hand-held reflectance spectrophotometer was used to record the colour of individual strips in order to make consistent and reproducible readings. Calibration was carried out using the yellow-blue axis $b^*(D65)$ value in the CIELAB1976 system to measure the colour of A-D strips suspended in enclosed containers over solutions of acetic acid in combinations with glycerol to control the relative humidity (RH). A-D strips were found to be sensitive to changes in high RH (60–90%) but affected little by changes in lower RH or temperatures in the museum display and storage range. A-D strips can be used to establish the presence of volatile acids, record the indication of acid vapour concentration, explore conditions within a container, and to find sources of volatile acidity. They respond very quickly and several can be placed around an object. They therefore show promise for measuring slowly changing conditions, such as seasonal changes and the gradual accumulation of acidity in poorly ventilated containers and spaces. A-D strips proved useful in assessing air quality in storage and display enclosures. Examples and test results are presented. Well-sealed plywood transit frames and storage cases were found to be most polluted with volatile acids. Storage rooms with air filtration systems but filled with wooden objects had significantly reduced air quality.

**Keywords:** Acetic acid, VOC, Vapour measurement, A-D strips, Calibration, Bromocresol indicator, pH, pKa, Ka, Spectrophotometer, CIELAB1976, Enclosure, Volatile, Pollution, Relative humidity (RH), Glycerol, Diffusion tube

**Introduction**

Volatile pollutants emitted from storage and display materials and other material in close contact with museum objects have been little studied, in part because of the difficulty of measuring them (Gibson & Brokerhof, 2001). The effect of the majority of volatile organic compounds (VOCs) emitted in typical storage conditions on materials in museum storage requires further research, but it is known that organic acids such as acetic and formic can cause damage to certain materials, such as lead (Tétérault et al., 1998, 2003), shells, and calcareous materials (Tennent & Baird, 1985; Brokerhof & Van Bommel, 1996), and other materials (Daniels & Ward, 1982; Andrew et al., 1993; Grzywacz & Tennent, 1994; Hatchfield, 2002; Ryhl-Svendsen, 1999–2002; Lavédrine, 2003; Grzywacz, 2006). In the past, priority has been given to the study of the stronger externally generated inorganic acid gases such as sulphur dioxide and nitrogen dioxide. In most countries, air pollution has been greatly reduced and improved museum design, frequently with air filtration, has been employed to prevent the ingress of externally generated pollution gases. Efforts to protect objects by glazing, casing, and portable storage have been shown to be both effective and economic, but well-sealed microclimates raise the concern that any internally generated pollutants could accumulate, exposing many museum objects to long-term damage (Padfield & Borchersen, 2007).

Diffusion tubes, passive samplers, and dosimeters provide proven methods for measuring concentrations of acetic (ethanoic) and formic (methanoic) acids in air (Clarke & Longhurst, 1961; Grzywacz & Stulik, 1992; Brokerhof & Van Bommel, 1996; Tétérault & Stamatopoulou, 1997; Gibson et al., 1997a, 1997b; Eremin & Wilthew, 1998; Ryhl-Svendsen & Glastrup, 2002; Grentoft, 2012; MEMORI project, 2013). However, analysis requires a long period of exposure (typically a month or two) and access to specialist skills and facilities (e.g. ion chromatography).
Consequently, they are expensive and are not used routinely. In the EU MEMORI project, two dosimeters, one sensitive to acid and the other to oxidation, were combined to develop a pollution sensor that measures both these damage modes (Dahlin et al., 2010; Grøntoft et al., 2010; Dahlin, 2013). Coated piezoelectric quartz crystals (pqc) have also been investigated as an alternative method of measurement of damage to specific materials from volatiles and other environmental factors (Odlyha et al., 2011). It has been observed that A-D (acid-detector) strips give a useful and quick visual guide to expected levels of volatile acids (Fenn, 1995; Hacke et al., 2014).

**Acid-detector (A-D) strips**

A-D strips were originally developed to measure the 'vinegar syndrome', the deterioration of cellulose acetate film stock leading to the emission of acetic acid. Currently, their main use is to monitor the storage of film stock by identifying any rapidly degrading cellulose acetate. The expected lifetime of degrading cellulose acetate has also been modelled and decisions to intervene can be taken.

A-D strips are based on an acid indicator which provides a colour change. The strips respond quickly to acid conditions, typically in one to two days at room temperature, depending on humidity and location, and could provide an economic alternative for more general pollution measurement, allowing museums to make many new and repeated measurements of storage and display conditions in order to develop a comprehensive picture of internally generated air pollution. Being essentially an acid indicator, they cannot be employed to identify a specific acid; also they can fade in strong light and are best used when exposed in the dark.

The manufacturers, the Image Permanence Institute (IPI), provide instructions for their use and a visual colour comparison, printed on a pencil provided with each packet (Fig. 1), which covers a range from blue through green to yellow, assigning a number (0, 1, 2, 3) depending on the severity of conditions. A small booklet with more information on the use of A-D strips is provided with each batch purchased from IPI, Rochester Institute of Technology (Appendix 1).

Danchek indicators based on the same principle are also available, though they have not been studied in detail here (Appendix 2). The present calibration does not apply to Danchek indicators, though a similar approach could be taken.

A-D strips must be stored in a well-sealed envelope from which light and circulating air is excluded. In use, they must be deployed cleanly (held with clean or gloved hands and if necessary attached and labelled at one designated end). Since, after removal from exposure to polluted conditions, the colour reverts quickly, they must be read immediately. A-D strips indicate the acidity present in the air and are not designed for surface pH measurements. They should not be allowed to become wet because their colour will run and if placed in direct contact with an absorbent surface might stain a museum object. This would also interfere with the reading.

A-D strips are made from bromocresol indicator for acid/base titrations. Bromocresol green is tetrabromo-m-cresol-sulfonphthalein (C₂₁H₁₄Br₄O₅S). In acid solution, at values below pH 3.8 it is in its yellow un-ionized form. Its blue ionized sodium salt is stable in solution at a pH higher than 5.4. This is called bromocresol blue. To make A-D strips, bromocresol green indicator is evenly deposited from solution onto rolls of paper in the presence of a small quantity of sodium hydroxide. The sodium hydroxide maintains a high pH before use and is formulated to extend the pH range during which a colour change occurs (Adelstein et al., 1995). When exposed to increasing concentration of acidic vapour the indicator changes from blue to green and eventually to yellow (Fig. 2). A-D strips are calibrated by matching their colour change to water-leached acid from film stock titrated against solutions of 0.1 N sodium hydroxide (Adelstein et al., 1995). Acetic acid has an acid hydrolysis constant \( K_a = 1.75 \times 10^{-5} \) and therefore bromocresol is a good match for the acetic acid range, changing colour from pH 5.4 to pH 3.8. For example, a 0.066% (w/w) solution of acetic acid in water (0.001 M solution) has a calculated pH of 3.87 in the liquid phase.

A study was carried out to explore the feasibility of employing a Minolta hand-held reflectance spectrophotometer to measure the \( L^*a^*b^* \) values of the diffuse reflections from A-D strips. It was observed that changes to both \( E \) (colour difference) and \( b^* \) (blue yellow axis) were useful direct measures of colour change, which are from blue to green in polluted museum conditions. Changes in \( a^* \) (red green
axis) do not give a useful response for the colour changes in A-D strips. The blue to green part of the spectrum corresponds with the conditions met during storage in museums. ΔE, which is the overall change incorporating changes in L*, a* and b* could also be used.

Issues to be addressed
Several questions were considered in relation to the use of A-D strips. Firstly, can small changes in acid vapour concentration be measured reliably using A-D strips? Are the results consistent and how should they be recorded? What is the best way of generating precisely known concentrations of acetic acid vapour? How do relative humidity (RH) and temperature affect the results? Can calibration results be translated into practical measurements? What types of conditions are they suitable to measure?

Equipment
In the current study, colour measurements were made on a hand-held Minolta CM 2600d spectrophotometer with a 3 mm diameter aperture, set to give results in CIELAB1976 colour space, using the standard 10° observer and CIE light source D65. The device was dark calibrated and then white calibrated on a CM-145 white reflection disc. Spectravite colour data software CM-S100W was used to control the instrument remotely and results were recorded for L*, a*, and b*. More details on the spectrophotometer are provided in Appendix 3.

Measurements of pH were carried out on a Hach Lange pH meter, details in Appendix 4.

Experimental
Initial tests were carried out using a range of dilute solutions, diluted from glacial acetic acid with deionized water, and used to partly fill (80–100 ml of solution in 1 l) sealed containers. Polypropylene containers were used, with lids sealed with polyethylene film and silicone high vacuum grease. Tests were carried out to measure the air-exchange rate of the containers using carbon dioxide gas and a logging detector (Fig. 3).

The containers were thoroughly cleaned, acidified with very dilute acetic acid and rinsed with distilled water, then left to dry. Around 100 ml of solution was used in each container, which produced stable conditions in the air space above.

Solutions were made up by weighing known amounts of glacial acetic acid to four decimal places and by adding deionized water to make up the weight to two decimal places for a specific concentration. Some of the diluted solution was then further diluted in the same way to create a range of concentrations by weight. A concentration range from 1% (w/w) to 0.0001% (w/w) was used. The pH of each resulting solution was measured. Calculated pH (see below) suggests that there is a little error in this process.

A-D strips were suspended in the air space above a solution using a cotton thread and/or a butyl rubber sealant known not to be a source of pollution. After two days, the colour change was measured and after a third day it was re-measured. From previous tests, this was found to be a reasonable time for conditions to become stable. Figure 4 shows the changes in reflectance b* against solution concentration in the range 0.025% (w/w) glacial acetic acid in water to 1%.

At lower concentrations, b* changes rapidly. Plotting b* against concentration gives a characteristic line close to a negative exponential at low concentrations up to 1% (w/w) acetic acid in water. When

Figure 2 Dilute solutions of bromocresol green in acetic acid at various concentrations. Lowest pH (more acid) on the left.

Figure 3 Carbon dioxide air exchange rate from a sealed 1 l polypropylene container, showing 0.604 air exchanges per hour, or a half-time of 69 minutes.
was plotted against log concentration a polynomial resulted, which was close to a straight line. The value \( b^* \) (D65) is preferable to \( \Delta b^* \) (D65) because as can be seen from Figs. 4 and 5, the value (in this case \(-33.5\)) for a fresh strip is at the steepest part of the curve and may vary more than other points. It is therefore better not to subtract it from all data in order to form a zero measurement as would be necessary for \( \Delta b^* \) (D65). Any discrepancy from the addition of sodium hydroxide in the manufacturing process or deterioration during storage is also thereby reduced.

The first measurements were carried out at room temperature (20.5°C) with the RH inside the container around 95% or more. This was measured using a datalogger to record RH and temperature (\( T \)) inside a container with zero concentration of acetic acid in water (Fig. 6).

Following these initial tests, the measurements could then be repeated over a range of values of RH...
relevant for a museum environment and equations generated for each value. Then \( b^* \) was re-plotted against calculated values of log percentage concentration resulting in the graphs in Figs. 7 and 8. These graphs can be used to calibrate the A-D strips across the range of RHs.

**Effect of RH**

To control RH in order to study its effects on the A-D strip response, experiments were carried out to explore the use of thick slurries of soluble salts, dissolved in water to produce a specific RH. The test showed that salts could give reliable and consistent RH conditions, however some salts could affect the A-D strips, for example, some acetates. It has also been suggested that magnesium nitrate might interfere with acetic acid measurements (Tétreault et al., 2003), although in these tests this salt appeared stable in the presence of acetic acid at room temperature. Rather than exploring this concern, an alternative means of producing known RH levels was employed by using specific weights of glycerol mixed with deionized water (Appendix 3).

Known weights of glycerol were added to the weighed solutions of acetic acid in water. It is assumed that glycerol reduces the evaporation rates of both water vapour and acetic acid. After some trials, it was decided that the glycerol mixtures gave consistent results. As well as being inert, the use of glycerol avoids the disadvantage of salt crystals being drawn up the side of the container by evaporation of the water. The disadvantage of glycerol is its viscosity, which reduces the precision of dispensing small amounts.

RH tests were carried out to create a complete set of calibration results of \( b^* \) (and \( \Delta E \)) against both solution concentration and RH at constant temperature (20.5°C). As can be seen in Figs. 7 and 8, the colour change response of A-D strips was greater at high RH, as might be expected, whereas there is very little difference between 53% and 62% RH (nor from 45% RH — more evident from Fig. 8). It was also observed that at low concentrations of acetic acid the effect of humidity is small.

**Effect of temperature**

The same calibration solutions were used to repeat selectively the readings at two further temperatures, 16.5 and 27.5°C. All the polypropylene containers were placed in an insulated box to reduce overnight temperature changes. The temperature in the containers at 20.5°C average varied by 1–1.5°C in a daily cycle, the 16.5°C set were carried out in an underground store with overnight changes less than 1°C and the high temperature measurements were the least stable (2–3°C). The three sets of results at different temperatures (Fig. 9) were similar and no trend was evident. It was concluded that temperature changes between 16.5°C and 27.5°C make very little difference to the colour response of the strips. This makes them convenient for the measurement of the effect of temperature on off-gassing by materials, which is thought to be significant across this temperature range.

**Practical details and sources of error**

It has been noted that errors in weighing acetic acid concentrations are small. For the RH calibration, glycerol was added by weight to the made-up solutions.
The viscosity of glycerol reduced the precision of handling for RH generation compared to making up acetic acid in water solutions. An RH and temperature logger was used to measure the actual RH over the period of the test (Fig. 10). This is only accurate to ±2%. The five newly purchased loggers were placed in an enclosure so that they were all exposed to identical conditions and their outputs compared before use and between each test. Even the one exposed to 92% RH remained in calibration for the duration of the tests. Glycerol / acid solutions were made up to produce specific RHs of 90, 70, 60, 50, and 40%. The measured values were 92, 72, 62, 53, and 45%.

Initially, a series of tests were carried out using a container with a slightly lower air-exchange rate ($T_{1/2}$ of 29.6 minutes) to explore and assess factors such as the effect of the height of suspension of the A-D strip above the solution, the concentration of acid solution and the RH level on the response time of the strip. Measurements demonstrate a 6 hour response half-time in the calibration containers, which means that after two days the colour change approached a stable level.

Repeated colour measurements of the same spot on a MacBeth ColorChecker chart were carried out to understand instrument error. Sixty measurements were made on a single spot producing a narrow range of results (Fig. 11).

In order to assess the variability across the strips, 100 measurements were carried out on different spots on several A-D strips. The standard deviation of this second set of measurements (Fig. 12) is much greater; therefore, any errors are largely associated with variations in A-D strips rather than with the reproducibility of the spectrophotometer.

The A-D strips came from one batch and therefore it was not possible to compare batch numbers for the strips. All measurements were carried out on lot #220008.

The above acetic acid measurements were repeated to a limited extent using formic acid solutions at various concentrations and RHs. Formic acid is a stronger acid than acetic with a $K_a = 1.78 \times 10^{-4}$, as discussed below.

**Calculating pH**

The law of mass action states that the rate at which a chemical reaction takes place at a given temperature is proportional to the product of the active masses of the reactants (Barrow, 1966, pp. 701–703). For dilute solutions, the term active mass approximates to the concentration in mol/l. Therefore,

$$K_a = [H^+] \times [CH_3COO^-]/[CH_3COOH]$$

For an electrically neutral solution, $[H^+] = [CH_3COO^-]$ we can simplify to

$$[H^+]^2 = K_a \times [CH_3COOH]$$

$$\text{pH} = -\log_{10}[H^+]$$

$$= -\log_{10}\sqrt{(CH_3COOH) \times K_a(\text{acetic})} \quad (2)$$

For acetic acid where $K_a = 1.75 \times 10^{-5}$, 1% (w/w) acetic acid = 0.1665 mol/l (0.1665 M).
Therefore, $[H^+] = 0.001707$ and $pH = 2.768$.

The calculated and measured $pH$ can be compared (Fig. 13) by using Equations 1 and 2. Aside from experimental error, differences between measured and calculated $pH$ may be due to the presence of small amounts of sodium hydroxide and the bromocresol indicator, particularly at low concentration.

At 62% RH, across the concentration range, formic acid behaved similarly to acetic acid within the accuracy of measurement (Fig. 14). There is some experimental deviation for very dilute solutions. In solution, based on its $pK_a$, formic acid solution is 3.64 times as strong as acetic, that is, the $[H^+]$ ion concentration in solution is 3.64 times higher for the same molar concentration. For solutions of the same $pH$ the effect of the vapour on the A-D strip was similar, suggesting that any differences in volatility do not alter the activity at the A-D strip significantly in the equilibrium conditions of a closed container.

### Practical use of A-D strips

Figure 15 summarizes the present calibration results plotted against calculated $pH$ of solutions of acetic and formic acids (at 20.5°C, before adjusting with glycerol to produce vapour of 62% RH).

| Example of museum container tested with A-D strips | $b^*(D65)$ Value |
|--------------------------------------------------|------------------|
| Empty hardboard container (deliberately constructed to be an emitter) | 34.14 |
| Collection paintings wrapped in transit frames (range of several tested) | 12.9–24.7 |
| Wooden drawer with paper objects in air-conditioned print room | 12.30 |
| Empty painting transport case, well-sealed, polyether foam | 11.37 |
| Glazed but poorly sealed empty painting frame | 7.75 |
| Empty sculpture storage and transport case, polyethylene foam | 5–6 |
| Empty non-archival solander box in filtered air-conditioned room | −2.42 |
| Old, damaged, and leaky solander box in filtered air-conditioned room | −1.86 |
| Q store (filtered air-conditioned but full of wooden storage cases) | −10 |
| Filtered air-conditioned print room | −28.09 |
| Unexposed A-D strip | −32.5 |

### Vapour concentration

This study provides a calibration of the A-D strips with respect to acetic acid solution strength and $pH$ but does not provide a direct or precise measure of the vapour concentration above the solutions. In the published literature, conversion factors are given for the vapour concentration above an acetic acid solution (Clarke & Longhurst, 1961; Brokerhof & Van Bommel, 1996; Tétreault & Stamatopoulou, 1997; Gibson et al., 1997a, 1997b; Hodgkins et al., 2008). Hodgkins has kindly provided calculated values of vapour concentration of acetic acid over solutions of known concentration at a variety of RHs (Hodgkins, 2014). Substituting these values for the solution
concentrations in Fig. 15 produces two graphs shown in Figs. 16 and 17. The $b^*(D65)$ A-D strip data at 92% and 53% RH are plotted against the logarithm of the vapour concentration calculated from Hodgkin’s data and also plotted on the same chart are colour measurements of the A-D strip comparison pencil, for zero concentration (blue), level 1 (cyan), level 2 (green), and level 3 (yellow).

As a comparison, the colour measurements for the A-D strip reference pencil and the values provided on page 10 of the IPI user’s guide handbook for air concentrations in parts per million are also plotted on the graph in Fig. 16 (ppm has been converted to micrograms per cubic metre). There are only four points available to be measured and therefore the data is presented as points rather than a line graph; it demonstrates that the two calibrations are compatible. The reference pencil measurements were made directly on a new pencil. The curvature of the pencil and printed nature of the colours introduce errors into these measurements; it was noted by measuring older pencils that the green dyes or pigments printed on the pencil are not entirely stable, so pencils used for comparison purposes should be stored carefully out of the light and comparisons restricted to the new pencils provided in each pack.

Some caution should be applied to the conversion of A-D strip colour change to vapour concentration since the calibration equilibrium conditions may not apply exactly to all readings taken in the field. Acetic acid, like water, is a volatile polar liquid and develops equilibrium with hygroscopic materials. When exposed, an A-D strip absorbs any volatile acid from the environment; the acid dissociates and reacts with small amounts of sodium hydroxide on the strip. The change of pH causes ionized blue bromocresol indicator to change towards the yellow un-ionized form. When removed from a container with a high acetic acid concentration, the A-D strip slowly reverts to a blue/green colour as the absorbed acid evaporates, but not to its original blue since some of the sodium hydroxide has been consumed. Reaction of sodium hydroxide with carbon dioxide takes place slowly and may be the cause of the permanent colour change. Field trials at very low concentration showed that A-D strips continue to change towards yellow during very long exposure (see below).

Case studies

Internally generated pollution in real museum conditions have long been known to have serious effects on specific types of objects but convenient methods of measuring and assessing risks are required (Toishi & Kenjo, 1968; Daniels & Ward, 1982; Zehnder & Arnold, 1984; Tennent et al., 1992; Andrew et al., 1993; Brimblecombe et al., 1999; Brokerhof, 1999; Blades et al., 2002; Ryhl-Svendsen, 1999–2002; Tétreault et al., 2003; Beltran & Maekawa, 2005; Odlyha et al., 2007; Schieweck & Salthammer, 2009). For many other materials used in museum objects, including cellulose, there is evidence that low levels of damage may be taking place as a result of exposure to high levels of relatively weak organic acids. Two approaches are required to assess the importance of volatile acid damage: by carrying out artificial ageing on materials in controlled conditions and by measuring actual conditions in storage and display.

In this study, in order to test the calibrations and to gain experience in their use, A-D strips were exposed as part of a survey of actual conditions in museum enclosures. The main concern was the levels of off-gassing in microenvironments such a storage cases for sculpture, enclosed painting frames, wrapped transit frames, solander boxes, and various storage cupboards. A-D strips were also used in combination
with diffusion tubes and dosimeters, such as the MEMORI dosimeter (Grøntoft et al., 2010), although these require different exposure times and were not be compared directly. In the calibration, A-D strips were exposed for at least three days at room temperature, though they can be left for a few days longer when necessary. When left in enclosures with other dosimeters that require two to three months exposure an apparently higher result than the calibration conditions was measured. The A-D strips therefore should be removed after seven days, though if used in conjunction with other dosimeters, this may interfere with the leakage rate of the enclosure. Very long-term tests beyond three months have been undertaken in order to investigate this aspect.

In order to obtain an overview of the practical performance of A-D strips, they were placed in various different types of containers in air-conditioned stores, choosing many containers suspected of being polluted (Rhyl-Svsendsen & Clausen, 2009).

A well-sealed empty painting case designed for transport, constructed from plywood with wood battens, painted on the exterior, containing polyether cushioning foam and rubber sealing gaskets but without an internal polyethylene sheet normally used to wrap the painting frame was chosen. Three A-D strips were exposed giving $b\ast(D65)$ values of 11.5, 10.6, and 12.0 after exposure. The average RH inside was 49.6% and the average temperature 23.7°C. The air-exchange rate was measured separately as 0.12 air exchanges per day (six days half-life).

In the newly built empty sculpture case, shown in Fig. 18, constructed essentially in the same way as the painting transit case, except using polyethylene foam, with an RH of 55% and temperature 21°C, eight A-D strips were located inside. The $b\ast(D65)$ values were consistently between 5 and 6 in the main container space, rising to 9.3 with close proximity to plywood. These cases typically have a low air-exchange rate, similar to the painting transit case (Fig. 19).

An empty non-archival solander box designed for storage of works on paper gave $b\ast(D65)$ values $-2.77$ and $-2.07$. Air exchange rates were measured to be 5.8 per day (2.9 hours half-life).

**Transit frames**

The highest readings are associated with polythene wrapped plywood transit frames. There is a wide range of results for the paintings stored this way, though for individual objects the results are repeatable. Variability in the wrapping process is a major factor, where well-sealed polythene increases the levels. Air exchange rates measured were between one air exchange per day for a very well wrapped transit frame and two per day for a more typical one. The plywood transit frame is clearly the main contributor to volatile acid emissions but the highest results are associated with objects painted on wood and board, suggesting that the museum object also plays a significant role in acid emissions (Bonaduce et al., 2012; Grøntoft et al., 2014).

**Painting frame backboards**

Glazed painting display frames are adapted to create microclimates by the addition of backboards. Two empty and almost identical painting display frames were given different backboards. The first frame had a design of backboard using oil-tempered hardboard covered on the inside with a thin sheet of Melinex (polyester film), a design which has been employed at Tate for many years. The initial A-D strip reading was $-33.5$ and the frame had an average $b\ast(D65)$ reading of 11.73. The second frame was given a polyvinyl chloride foam backboard, which was expected to be a low emitter. The average $b\ast(D65)$ reading was...

![Figure 18 Initial condition of two A-D strips exposed over three days. Within the main volume of an empty case, colour changes tend to be similar. Small but significant differences were measured between the two strips (shown here), one in greater proximity to a source of volatile acidic pollution (plywood).](image1.png)

![Figure 19 Some typical case study measurements plotted on the trend line of the 53% RH calibration graph. Adding carbon cloth reduces acid levels to less than $-20$, demonstrating one mitigation option.](image2.png)
The new backboard was therefore a significant improvement in this respect. The original frame rebate is presumed to cause the remaining organic acid emissions. Next, two identical polyvinyl chloride backboards were compared, using the same two frames, except one had the addition of carbon cloth inserted in front of the backboard. The results were $-1.53$ for the control frame and $-27.03$ for the carbon cloth. The addition of carbon cloth gave an excellent result suggesting that, together with a non-emitting backboard, it could improve conditions significantly within an existing painting frame. Air exchange rates for the glazed frames varied between 2.6 per day for a screwed only backboard to 1.9 per day for a backboard further sealed with paper tape. The A-D strip measurements were carried out on empty frames to investigate ways of improving their design, however it should be remembered that the stretcher and painting itself are sources of volatile acids and will add further to total VOC levels.

Photographic negative store

Photographic negatives stored, tightly packed, in individual Manila hanging folders in six metal cabinets, each with four horizontal rows, were observed to have a slight vinegar smell.

Fifty-two A-D strips were exposed for two weeks, distributed throughout the negatives storage cabinets, and measurements made. The graph in Fig. 20 shows the frequency of occurrence of colour measurements across the range of results. This is not a normal distribution, indicating that several sources of pollution are spread throughout the cabinet. Air exchange rates were not measured, but can be estimated to be in the order of 10 per day. Not all readings are high though and there is a relatively random spread, suggesting that a minority of the negatives are sources of acetic acid (e.g. cabinet 3, shelf 2) and that many may not be in poor condition. It may be possible to identify a limited number of negatives to be re-washed in order to reduce the problem. Alternatively, the use of sorbents could be considered, though this would require re-housing the negatives in larger cabinets. Increasing ventilation would help but would involve moving the negatives to a less accessible location. The results of this study will also influence plans for digitization.

Anoxic frame

A design of anoxic frame for works on paper, developed at Tate, is made from glass and aluminium, with a butyl rubber sealing gasket. In addition, a two-pack polyester was applied outside the glass sealing gasket, which raised concerns of a possible pollution source (Townsend et al., 2008; Strlic et al., 2011). The frame has a measured oxygen inward leakage rate of 1–2% in one year. A-D strips were placed inside an empty anoxic frame and left for two weeks. The frame was not filled with nitrogen. The A-D strips were from a new batch and had a higher initial $b^*(D65)$ value of $-37.5$. They changed colour from blue, $b^*(D65) = -37.5$ to blue-green, $(b^*(D65) = -18.7)$. Although in many circumstances this might be considered a good result, the necessarily very low air-exchange rate of the anoxic frame and its small volume ($4500 \text{ cm}^3$) raises the likelihood of long-term accumulation of any pollutant.

A sample of gasket was placed in a clean glass vial with an A-D strip, using an empty vial as a control. The A-D strip in the vial with the gasket turned blue-green, but less so than in the anoxic frame ($b = -31.3$ after two days, $-21.6$ after one month) when conditioned to 60%RH. The interpretation is that the gasket emits a very low amount of volatile acid and there is also a second source, which may be the two-pack adhesive emitting sufficiently to penetrate or react with the gasket. Other material sources of pollution are unlikely since the frame is made from glass and aluminium, but release coatings could also be responsible. The rate of air exchange of the vial is probably greater than that for the anoxic frame; therefore, the difference may also be explained by better ventilation of the vial. The difficulty of identifying the relative contribution of all sources of pollution has been observed for other containers.

An old degraded newspaper dated 21 July 1969 (and kept since in a series of wooden drawers) was inserted in the anoxic frame with A-D strips. Again, nitrogen

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**Figure 20** Distribution of A-D strip readings over a range from $b^*(D65) = 6.8–23.7$. Exposures carried out in six photographic negative cabinets. The wide spread in this graph combined with the location of high readings suggest more than one localized source of pollution.
was not introduced. The A-D strips all turned green in two weeks (average \(b^* = -12.4\)). This confirms that any degraded work of art put into the frame is likely to be a source of pollution, and most will be more highly emitting than the gasket. A carbon cloth was then inserted in the anoxic frame with the newspaper and A-D strips. After five months the A-D strips remained blue, although without measurement (which would have involved opening the frame), it is not possible to say that they are entirely unchanged. The frame remained closed and stored in a cupboard in the dark. After 17 months, the frame was opened and measured. An initial reading of \(-37.5\) had fallen to \(-36.5\) on the carbon cloth, \(-36\) on the glass, \(-34\) on the aluminium backing, \(-32.5\) on the newspaper were measured. These readings are very close to zero, although the tiny differences between them appear to be significant. Presumably all pollution and even carbon dioxide was removed from the small air volume within the frame. Since an anoxic frame is designed to remove sources of degradation, it should therefore always contain a sorbent such as activated carbon.

**A-D strips Tate stores sequence to measure longer term changes**

A-D strips were exposed in air-conditioned and filtered stores containing various works of art in storage. Eight locations were chosen, in four glass and metal storage cabinets in Q store; in Q store on top of a cabinet open to room conditions; in S store and U store on painting screens; and in an adjacent unconditioned corridor. Two readings were taken (one on each side of the strip) after one week and then a second strip was deployed at each site. This continued until eight strips were at each site. The strips were read at intervals over 150 days, making a total of 1200 readings.

After one week, individual strips had reached a relatively stable state but the \(b^*(D65)\) value continued to increase over the next 200 days, though at a much slower rate (Fig. 21). The evidence is that the rate of increase is slowing. Fig. 22 shows results for the first set of A-D strips at sites in Q store and three of the cabinets. The data from the fourth cabinet is omitted because the cabinets were opened and emptied, interfering with monitoring. Results for the fourth cabinet and the two painting stores are similar to those in Q store.

The levels for Q store were marginally lower than in the three cabinets (111, 116, 126), which had poorly sealed sliding doors. Air exchange rates for the cabinets have not been measured; an estimate would be in the order of 10 per day. The cabinets contained small sculptures, visibly displayed on shelves. The very small difference between the cabinets and the store room is evidence for low emissions from the objects inside and a high air interchange with the store room. The overall levels in the store are high \((b^* > -10)\) for a filtered and air-conditioned space, which is attributed to high levels of emissions from other packed material in the very full Q store, mainly wooden cases containing sculpture. The results for S and U painting stores also reveal relatively high levels of off-gassing from materials stored densely on screens, all in transit frames.

The behaviour of the A-D strips in Q store is interpreted as an initial response to volatile organic acids followed by a slow reaction of carbon dioxide and pollutants in the air with the sodium hydroxide on the strip. For comparative purposes with other short period measurements, the most useful readings of pollution levels are those made after one week.

**Some general results from the case studies**

A-D strips were used to survey a number of different storage methods and to assess the relative significance of volatile organic acids in each. They proved useful in identifying and characterizing specific problems as well as providing an overview (Baker, 2011). The
ability to make many accurate measurements gives confidence in the outcome and exposure periods of about one week are stable. A-D strips proved useful for analysing the localized variation in polluted conditions within different display and storage cases and therefore can be used to investigate the effectiveness of methods to protect enclosed museum objects from internally generated pollution by using barriers, sorbents and other remedial measures (Brokerhof, 1999; Schieweck & Salthammer, 2009). Since A-D strips respond in days, they should also be useful in measuring conditions in enclosures where seasonal temperature and humidity changes have a significant effect on the emission rate and activity of pollution.

Three A-D strips can be used for each measurement in case one becomes contaminated or otherwise gives an anomalous result. Separate readings can be taken from each side of one strip using the 3 mm diameter aperture of the spectrophotometer. Depending on location, the readings can then be averaged or the difference used to locate pollution sources. Many more readings can be taken from one strip, if considered useful, however the number may be limited by colour-reversion time-constraints, particularly at higher concentrations. Colour measurement must be made immediately by taking the instrument (and any software) to the container and preparing to measure swiftly. When making more than one reading, there is no time to pause. After removal from a polluted container, repeat readings are always lower than the first reading. Alternatively, a large number of A-D strips could be exposed and removed individually. When handling A-D strips, they can be held at one end, keeping the rest of the strip clean. The handled end can also be used for fixing and labelling, when necessary. By tying one end to a long thread for easy removal, A-D strips can be withdrawn from an enclosure without disturbing conditions inside.

Some A-D strips have been exposed in open store rooms. Provided there are no local draughts they can be used to check the state of air-conditioning filters or to measure any accumulation of volatile acid pollution in a very full store. In these cases, they can be read in situ. Readings taken after the first week continued to rise and are therefore less reliable. In these trials, A-D strips have not been used in open gallery conditions where air movement is greater and external pollution may interfere with interpretation of results.

A-D strips were placed in glass vials enclosed with various individual materials conditioned to 60% RH in order to assess the emission behaviour of these materials for use in frames and cases. This is similar to an Oddy test (Green & Thickett, 1993, 1996). They show promise in this area and a protocol could be developed.

When used in very small spaces, it is important to preserve some air space around the strip otherwise not enough volatile acid reaches it, for instance, lower readings occur between pages of a book or in direct contact with a material. This aspect deserves further study in combination with the study of the behaviour of pollution barriers. Placing a strip in a Melinex envelope then flattening it to remove most of the air prevents the A-D strip from changing significantly (in the absence of strong light). This is a useful way of transferring an A-D strip from an inconvenient exposure location to a place for colour measurement and also of preserving strips for later use, as is flattening under layers of aluminium kitchen foil.

In enclosed spaces, differences in colour between the two sides of an A-D strip can be used to locate a suspected source of pollution and to identify the direction of flow of pollutant. An interesting observation is that in contact with activated carbon cloth one side of an A-D strip can remain blue when the exposed side has changed colour, possibly very significantly.

**Conclusions**

Consistent and reproducible results can be achieved by using A-D strips to measure volatile acidic pollution within enclosures by using a reflectance spectrophotometer to record their colour more accurately. Calibration has been carried out using the $b^*(D65)$ value in the CIELAB1976 system to measure the colour of A-D strips suspended in enclosed containers over separate dilute solutions of mainly acetic acid (and also some formic acid) diluted in de-ionized water and with glycerol added to control the RH of the air above. A-D strips were found to be sensitive to changes in high RH (60–90% RH) but affected little by changes in low RH and by temperatures in a broad museum range (16.6–27.5°C). Results were compared with passive samplers and previously published studies using diffusion tubes and were found to be broadly consistent, though not directly comparable as vapour concentrations.

A-D strips do not provide direct readings of vapour concentration in air but they do provide useful information on the activity and concentration of volatile acids at specific points that are in close proximity to an object, and they can be deployed in order to find the sources of volatile acidity. They also respond quite quickly and, since they are small and inexpensive, several can be placed around (but not touching) an object for increased accuracy or to observe any variations. They show promise for the measurement of changing conditions, such as seasonal changes, and for understanding any gradual accumulation of acidity in poorly ventilated areas and containers. A consistent and detailed picture of museum volatile.
acidity conditions is being developed from the accumulated A-D strip readings.

In combination with other methods of measuring volatile acids, such as the MEMORI dosimeter (Grøntoft et al., 2010) or diffusion tubes, A-D strips can provide a detailed and localized studies of volatile acid pollution conditions in low air exchange buildings and in storage and display containers. In combination with micro pH measurements of samples from objects, they allow a distinction to be made between volatile and bound acids, offering the possibility to study the transfer of acid pollutants through materials and museum objects.

Specialist conservation products are rarely developed, but fortunately A-D strips are already manufactured for related monitoring and therefore available. Acid/base indicators appropriate for the detection of other pollutant gases, such as nitrogen oxides, could also be useful, for conservation and also other environments, and oxidation/reduction (redox) indicators might also be worth considering.

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Appendix 1 A-D strips supplier
Image Permanence Institute, IPI, Rochester Institute of Technology, 70 Lomb Memorial Drive, Rochester, NY 14623-5604, USA. www.imagepermanenceinstitute.org

Appendix 2: Danchev strips supplier
Dancan International Sales, Box 308, 1501 Copenhagen V, Denmark. Tel.: +45 4050 4180, Email: Dancan@email.dk.

Appendix 3
Minolta spectrophotometer CM 2600d with a 3 mm diameter aperture set to give results in CIELAB1976 colour space, using the standard 10° observer and CIE light source D65. The light source is a xenon lamp filtered to give a wavelength range from 360 to 740 nm, with a 10 nm interval between data points, dispersed by diffraction grating. 100% UV range was selected. The light-receiving element is a silicon photodiode array (dual 40 elements). Illumination is d/8 (diffuse illumination, 8-degree viewing). Simultaneous specular gloss inclusive and exclusive (SCI and SCE) measurements were made. For a matt surface such as A-D strips the differences are small. The device was dark calibrated against a distant non-illuminated background and then white calibrated on a CM-145 white reflection disc. Three readings are made for calibration, set on SCI and SCE, 100%, and 3 mm (SAV) using a target mask Φ3 mm. Spectra-Magic NX colour data software CM-S100W was used to control the instrument remotely and results were recorded for \( L^* \), \( a^* \) and \( b^* \). Normally, single sample readings were made on both sides of an A-D strip.

Illuminant: A, C, D50, D65, F2, F6, F7, F8, F10, F11, F12 (simultaneous evaluation is possible using two light sources).

The observation system conforms to CIE No. 15, ISO 7724/1, ASTM E1164, DIN 5033 Teil7 and JIS Z8722 Condition C standard.

Observer: 2/10° (CIE 1931/2°, CIE 1964/10°).

Colour space/colorimetric data.

\( L^*a^*b^* \), \( L^*C^*h \), CMC (1:1), CMC (2:1), CIE94, Hunter Lab, XyY, Munsell, XYZ, MI, WI (ASTM E313), YI (ASTM E313/ASTM D1925), ISO brightness (ISO 2470), density status A/T, WI/Tint (CIE/Ganz), CIE00.

Spectral reflectance: Standard deviation within 0.1% (360–380 nm within 0.2%).

Colorimetric value: Standard deviation within \( \Delta E^*ab \) 0.04.

Measurement conditions: White calibration plate measured 30 times at 10-s intervals after white calibration was performed.

Appendix 4 Hach Lange pH meter
Portable waterproof battery operated H160 meter with 4 mm diameter ISFET pH probe, accuracy 0.01 pH units, resolution 0.01 units, calibration points pH 4.01 and 7.00. Operating temperatures range up to 45°C.

Appendix 5
Glycerol/water mixtures percentage by weight

| RH% | Glycerol (g) | Water (g) | Specific gravity |
|-----|-------------|-----------|-----------------|
| 10  | 95          | 5         | 1.245           |
| 20  | 92          | 8         | 1.237           |
| 30  | 89          | 11        | 1.239           |
| 40  | 84          | 16        | 1.216           |
| 50  | 79          | 21        | 1.203           |
| 60  | 72          | 28        | 1.184           |
| 70  | 64          | 36        | 1.162           |
| 80  | 51          | 49        | 1.127           |

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