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# Magnesium nitrate as sustainable solution for constant RH (53%) and pollutant absorption in display cases



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The Viking Ship Museum Oslo started in 1957 using saturated salt solutions (here calcium nitrate) to stabilise the relative humidity (RH) in display cases. Three decades later, excellent results with low effort and cost were reported. However, many museums have since replaced these solutions with preconditioned silica gels. Their much lower water capacity causing more frequent need for maintenance, shifting equilibrium RH, unreliability as pollutant absorbers, and possible contamination were not considered or unknown at the time. The absorption capacity of saturated magnesium nitrate solutions for corrosive pollutant traces was studied using metal-oxide-semiconductor (MOS) gas sensors. Corrosive carbonyl pollutants (formic and acetic acid, formaldehyde, and acetaldehyde), often emitted from wood, are indeed highly absorbed. Some absorption was also demonstrated for hydrogen sulfide and sulfur dioxide. Practical application tests worldwide in museums have confirmed the advantages of this sustainable and failsafe passive method.

Controlling the relative humidity (RH) in the environment of objects is a major concern in preventive conservation. Saturated salt solutions achieve a fixed RH in closed chambers (ISO 483) and are used, for example, to calibrate hygrometers. Conservators are familiar with their use in humidification chambers for organic objects<sup>1</sup> or for controlled drying. In 1957, the Viking Ship Museum Oslo was the first to use such solutions in display cases (calcium nitrate, deliquescence RH (DRH) = 53.7% at 20 °C)<sup>2</sup>. After three decades, excellent results at low effort and cost were reported<sup>3,4</sup>. Despite large fluctuations in the exhibition hall (RH = 25–85% at temperatures between 17.5 and 22.5 °C), the RH in the not very tight display cases fluctuated only between 48% and 62%<sup>3</sup> and was mostly in the range of 50–60%<sup>4</sup>, meeting the standard requirement of  $55 \pm 5\%$  for mixed collections. The finds displayed together with wood (bronze and iron) were in good condition after 30 years (no corrosion). The ‘creeping’ of salts could be avoided by choosing suitable container materials like polyethylene<sup>4</sup>. Creahan<sup>5</sup> took up the idea and experimented also with calcium nitrate; she covered the containers with a polytetrafluoroethylene membrane.

Surprisingly, only a few people have followed this approach. As RH preconditioned silica gel became available after 1990, solutions were replaced in some museums because easier handling was assumed. However, silica gels have disadvantages, such as a lower water capacity per weight of absorbent (meaning more frequent maintenance is needed), the shifting of RH with water content, and (not considered or investigated at the time)

unreliability as pollutant absorbers<sup>6</sup>. In addition, even unused silica gel can be contaminated: model glasses corroded over conditioned silica gel fresh from the supplier, and the gel indeed caused corrosion in an Oddy test, mainly on lead<sup>7</sup>. Therefore, silica gel needs to be decontaminated, but normal drying and reconditioning are not sufficient<sup>8</sup>. A tested protocol for museum use (possibly, heating over more than 100 °C for hours and reconditioning afterwards) seems not to exist and would be impossible to apply with the readymade PRO SORB cassettes (<https://www.talasonline.com/images/PDF/ProductInformation/Prosorb-brochure.pdf>) made of polypropylene and polyester fleece, which are often used.

For our tests, magnesium nitrate hexahydrate (RH = 54.4% at 20 °C, known as garden fertiliser and mineral nitromagnesite in bat guano caves), was selected for two reasons: first of all, the RH shifts by only  $\pm 1.5\%$  for a temperature change of  $\pm 5$  °C instead of the chemically similar calcium nitrate (ca  $\pm 3\%$ ) used in Oslo (Table 1).

Secondly, it has already been used successfully for approximately two decades in Boston at the Fiske Center and the Harvard Museum of the Ancient Near East<sup>9</sup> (cupboard with organic finds, display case with ancient Egyptian mummy cartonnage) and Germanisches Nationalmuseum Nürnberg (GNM, D) (an inlaid wooden portrait from the Röntgen Workshop, information by A. Dix 2023). In the GNM, the application of this solution for climate control of organic materials was demonstrated to the public in the exhibition ‘Anti-Aging for Art’<sup>10</sup>. The use of magnesium nitrate was pioneered

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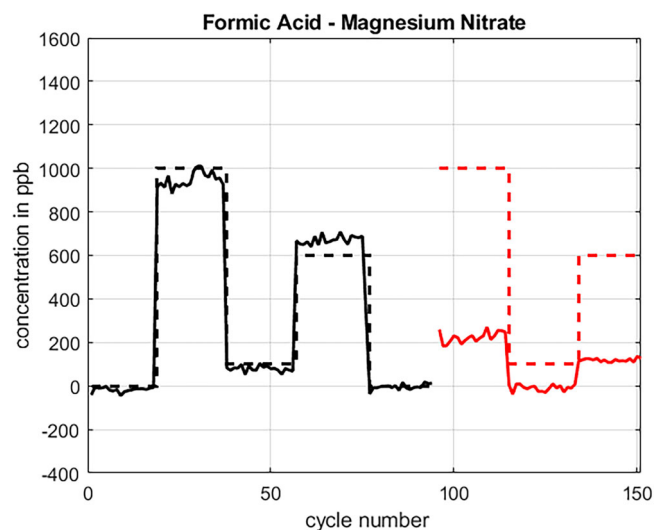
**Table 1 | Deliquescence relative humidities (DRH) at various temperatures<sup>23</sup>**

| Compound                      | Formula  | 15 °C  | 20 °C  | 25 °C  | 30 °C  |
|-------------------------------|--|--------|--------|--------|--------|
| Magnesium nitrate hexahydrate | Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 55.87% | 54.38% | 52.89% | 51.40% |
| Calcium nitrate tetrahydrate  | Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O | 56.89% | 53.67% | 50.74% | 48.07% |

**Table 2 | Data for Henry's Law constants, first (=best) value**

| Pollutant            | $H_s^{cp}$ [mol/(m <sup>3</sup> ·Pa)] | $H_s^{cc}$ |
|----------------------|---------------------------------------|------------|
| SO <sub>2</sub>      | 0.013                                 | 32         |
| NO                   | $1.9 \times 10^{-5}$                  | 0.047      |
| NO <sub>2</sub>      | $1.2 \times 10^{-4}$                  | 0.30       |
| HCOOH                | 88                                    | 220,000    |
| CH <sub>3</sub> COOH | 40                                    | 99,000     |
| HCHO                 | 32                                    | 79,000     |
| CH <sub>3</sub> CHO  | 0.13                                  | 320        |
| H <sub>2</sub> S     | 0.001                                 | 2.5        |
| HCl                  | 15                                    | 38,000     |
| HNO <sub>3</sub>     | 880                                   | 2,200,000  |
| CO <sub>2</sub>      | $3.4 \times 10^{-4}$                  | 0.84       |

Conversion to  $H_s^{cc}$  according to  $H_s^{cp} = 1 \text{ mol}/(\text{m}^3 \cdot \text{Pa})$  is equal to  $H_s^{cc} = 2478.96$ .

**Fig. 1 | Formic acid (methanoic acid, HCOOH).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response, difference of red curves demonstrates the absorption.

by Susanne Sack<sup>11</sup> in 1963, who described the construction of an exhibition case for the panel painting on loan, *The Adoration of the Shepherds*.

When mixing 2.5 kg magnesium nitrate hexahydrate with 1 L water, half of the salt remains undissolved. Therefore, such a mixture can absorb another litre and remain saturated. On the other hand, evaporating 1 L is enough to humidify ca 190 m<sup>3</sup> dry air (heating period) from RH = 30% (i.e. 6.9 g/m<sup>3</sup> absolute humidity) to 52.9% (12.2 g/m<sup>3</sup>). As long as at least one drop of solution is present in the display case, the RH does not shift. Only then would maintenance (here, adding water) be required. For comparison, 2.5 kg of PRO SORB, a silica gel frequently used in museum display cases, conditioned to 52.9% RH, contains 821 g of water (<https://www.talasonline.com/images/PDF/ProductInformation/Prosorb-brochure.pdf>).

However, for silica gel, the equilibrium RH decreases with decreasing water content. After using 103 g (humidification of approximately 19 m<sup>3</sup> dry air), the equilibrium RH would deviate by more than 5% from the set value. Therefore, silica gel is not well suited for display cases in rooms without an HVAC system. It would require very frequent maintenance, extremely tight cases, or a high amount of silica gel. Thomson<sup>12</sup> calculates 20 kg (=27 L) per m<sup>3</sup> for a 'well-made case' with an air exchange rate (AER) of 1/day, while the supplier of PRO SORB provides as 'guidelines' just 2–4 kg.

The corrosion of exhibits by pollutants in display cases is still a matter of concern and research in preventive conservation. It is not only the familiar tarnishing of silver<sup>13</sup>; recent examples investigated at the Stuttgart Art Academy are various calcium acetate efflorescences formed on calcareous objects by acetic acid from wood<sup>14</sup> ('Byne's disease'), 'black spots' on bronzes<sup>15</sup> due to sulfurous gases, and glass-induced metal corrosion by formaldehyde<sup>16</sup>, etc.

Are gaseous pollutants partially absorbed by solutions, as predicted by Henry's Law? Henry's Law states that the amount of dissolved gas in the liquid is proportional to its partial pressure in the gas phase. The proportionality factor is known as Henry's Law constant. These factors are listed for pure water<sup>17</sup>.  $H_s^{cp}$  are the Henry's Law constants with the aqueous concentration measured in mol/m<sup>3</sup> and the partial pressure in Pa. These can be converted for  $T = 298.15 \text{ K}$  and a solution density of 997 kg/m<sup>3</sup> to  $H_s^{cc}$ , which is the ratio of the molar concentrations in the aqueous and gaseous phases. This is equivalent to the particle ratio.  $H_s^{cc} = 32$  (for SO<sub>2</sub>, see Table 2) means that for every molecule in the gas phase, there are 32 molecules dissolved in water (when volumes of the same size are compared).

Polar pollutants prefer water to the gas phase: Table 2 shows that pure water is an excellent absorber of organic and mineral acids and short-chain aldehydes. It also works for SO<sub>2</sub> but not very well for nitrogen oxides. H<sub>2</sub>S can be found in both phases.

Compared with pure water, the water activity of a saturated salt solution of magnesium nitrate (DRH = 52.9% at 25 °C) decreases from 1.0 to 0.529. The ability to dissolve pollutants will decrease accordingly. Unfortunately, data for salt solutions are almost completely missing. Therefore, the absorption capacity had to be determined experimentally.

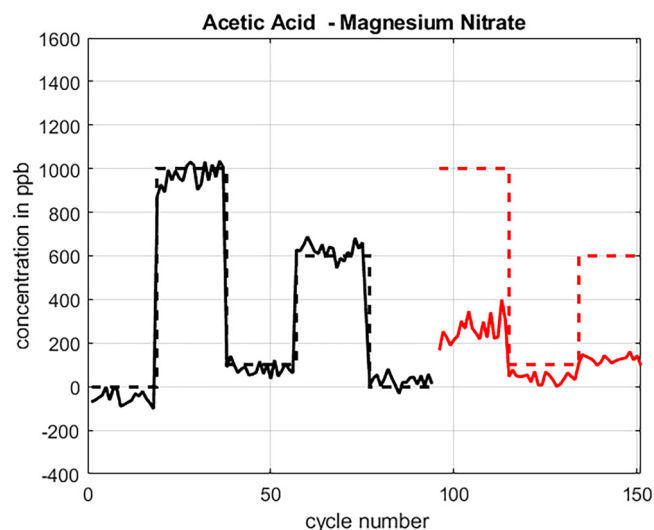
## Methods

### Method of static gas measurements

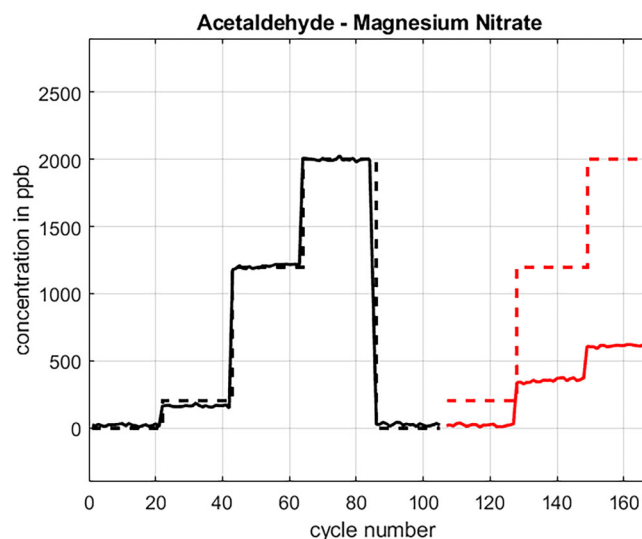
Metal-oxide-semiconductor (MOS) gas sensors allow the continuous monitoring of relevant trace gas concentrations in the gas headspace of a bottle partially filled with a test solution. In all, 10 ppm of acetic acid, formic acid, or hydrochloric acid was injected in a 2 L bottle with 200 mL salt solution. The concentration was chosen orders of magnitude higher than what one typically finds in display cases to evaluate if, even then, absorption works. The concentration was achieved by injecting a calculated volume of gas from the headspace of a vial with concentrated acid. The absorption was followed by an SGP40 sensor (Sensirion, Stäfa, Switzerland), which contains four different sensors with different sensitive layers (see Fig 4 in ref. 19). In static operation, the sensors measure the surface conductance, which depends on the trace gas concentration but cannot be assumed to be directly proportional. Since each sensitive layer reacts differently towards each substance and concentration, the change of all four layers can be used to achieve some form of selectivity. Schütze and Sauerwald<sup>18</sup> described the dynamic operation of MOS gas sensors. The benefit of this method is a higher sensitivity as well as a better selectivity. The temperature cycle in the static gas measurement results in a reading every 30 s and is further explained in ref. 20.

### Method for dynamic gas measurements

In another setup, pollutants were supplied by a continuous flow of 500 mL/min through a bottle with 200 mL gas headspace over 300 mL of solution. This means that after 24 s, the gas volume in the headspace is completely exchanged and the salt solution is constantly supplied with more pollutant of the set concentration to absorb. If the sensors measure a



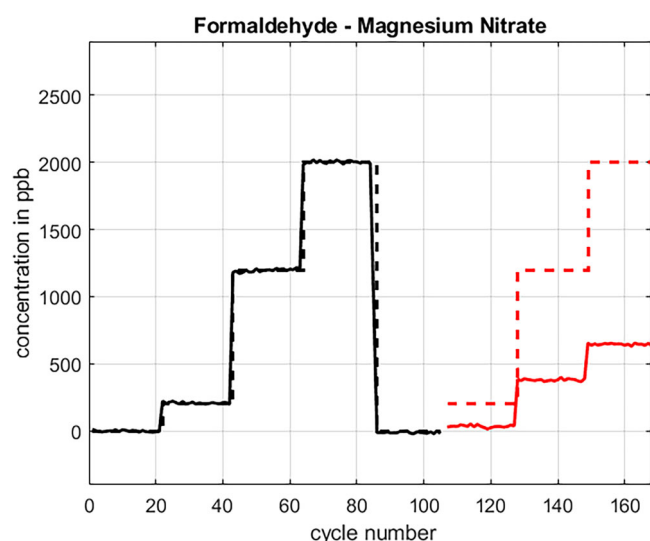
**Fig. 2 | Acetic acid (ethanoic acid,  $\text{CH}_3\text{COOH}$ ).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response. Difference of red curves demonstrates the absorption.



**Fig. 4 | Acetaldehyde (ethanal,  $\text{CH}_3\text{CHO}$ ).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response. Difference of red curves demonstrates the absorption.

**Table 3 | Half-life time  $T_{1/2}$  for absorption of 10 ppm acid by saturated magnesium nitrate solution**

| Acetic   | Formic   | Hydrochloric |
|----------|----------|--------------|
| 6.22 min | 4.09 min | 9.51 min     |



**Fig. 3 | Formaldehyde (methanal,  $\text{HCHO}$ ).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response. Difference of red curves demonstrates the absorption.

continuous reduction of the set concentration after contact with the saturated solutions, an absorption of high volume is evident. These extreme conditions were selected to determine whether absorption could be demonstrated even then.

For each pollutant, three different trace concentrations (see Figs. 1–6 for details) of some 100 ppb over the solution were supplied using a specially constructed gas mixing apparatus (GMA). Measurements using five different sensors with 11 different sensitive layers were also performed using empty bottles and pure water for comparison. One data point was generated

for each temperature cycle of 144 s. For further experimental details, see refs. 19,21.

## Results

### Results for static gas measurements

The decay of the electrical signal (see Fig. 4 in ref. 19) could be fitted exponentially and yielded half-life times  $T_{1/2}$  in the range of a few minutes (Table 3), demonstrating that the pollutants are readily absorbed even without any ventilation.

### Results for dynamic gas measurements

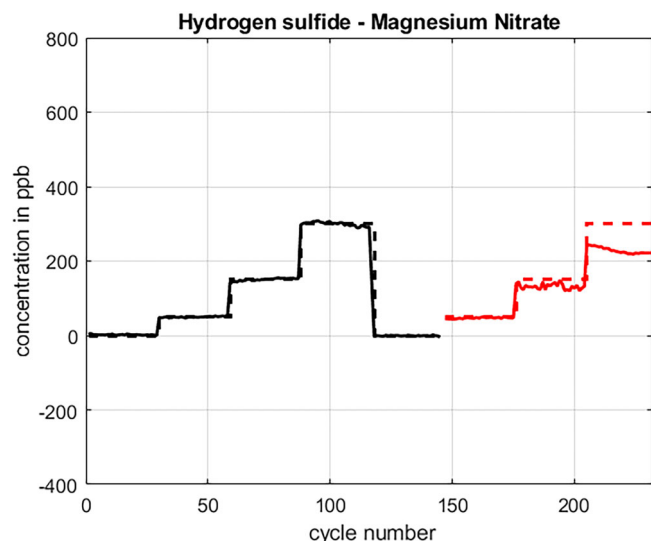
The results are shown in Figs. 1–6. The black lines refer to the sensor training without the salt solution. The dashed line indicates the concentration of the gas flow provided by the GMA. The solid line shows the sensor response after training the sensors. The better these black curves match, the better the training (see, for example, Fig. 3). The red lines indicate the effect of the salt solution. The deviation of the full red line (sensor signal) from the dashed line (concentration provided) proves the reduction in the pollutant concentration by absorption. For example (Fig. 1), the concentration provided of 1000 ppb (=1 ppm) formic acid was reduced to ca 250 ppb, that of 100 ppb was close to 0, and that of 600 ppb to ca 100 ppb.

## Discussion

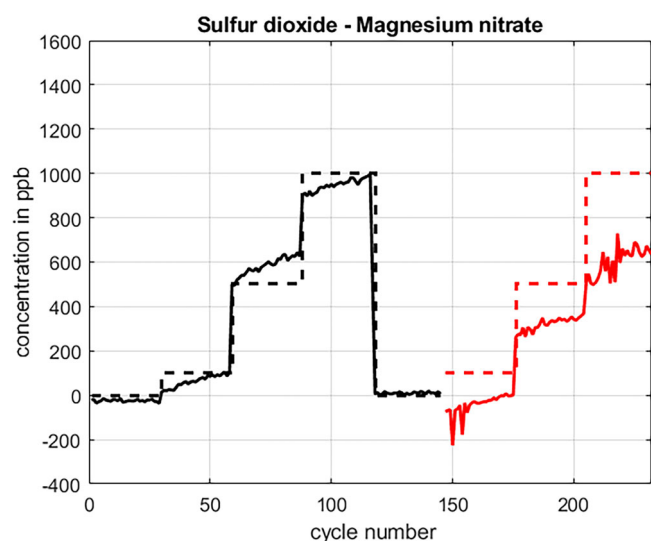
As expected from the Henry coefficients for the distribution of compounds between the water and gas phases (Table 2), corrosive polar compounds such as carbonyls emitted from wood (acetic and formic acids, acetaldehyde, and formaldehyde) prefer the aqueous phase; they are highly absorbed by the magnesium nitrate solution. For formaldehyde, this was also tested successfully in a not very tight display case (see Fig. 6 in ref. 19, light blue curve) and in a hermetically sealed emission chamber (1 m<sup>3</sup>, still air, half-life time for absorption of 100 µg: ca 50 min<sup>22</sup>).

The Henry coefficients  $H_s^c$  (Table 2) for hydrogen sulfide and sulfur dioxide are much smaller (<50). Nevertheless, some absorption was also observed when the pollutant was supplied by continuous flow (Figs. 5 and 6). Under real-life conditions in display cases, the immission of pollutants into the air is much smaller, and there is much more time for absorption; therefore, much better results are to be expected.

However, the sensors did not deliver unambiguous interpretable results for nitrogen dioxide, hydrogen chloride, and carbonyl sulfide (carbon oxide sulfide, COS). The reasons for this are not evident. While the



**Fig. 5 | Hydrogen sulfide (H<sub>2</sub>S).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response. Difference of red curves demonstrates the absorption.



**Fig. 6 | Sulfur dioxide (SO<sub>2</sub>).** Black curves without, red curves with salt solution. Dashed: concentration provided by GMA, full curve: sensor response. Difference of red curves demonstrates the absorption.

sensor training worked for NO<sub>2</sub> and COS, the signals in the presence of the solution were higher than the concentration provided by the GMA. Which interaction in the gas phase is responsible for that is unclear. The trace equilibrium emission of 0.17 ppb HNO<sub>3</sub> from the solution (see below) caused no problems with the other gases. For hydrogen chloride, no stable sensor response was achieved, which led to a poor quality of the model building. However, the absorption of hydrogen chloride was clearly demonstrated in the static experiment (Table 3). Carbonyl sulfide is known to hydrolyse in aqueous solutions according to  $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$ . As shown, the reaction product H<sub>2</sub>S is absorbed to some extent. H<sub>2</sub>S re-emitted into the gas phase might interfere with the sensors.

Ozone (O<sub>3</sub>) and nitrogen monoxide (NO) were not tested because of their short half-life time indoors. Except for NO<sub>2</sub> and carbonyl sulfide, the absorption of all other tested corrosive pollutants was demonstrated. Therefore, the use of saturated salt solutions in display cases can help

avoid pollutant-induced corrosion of exhibits additionally to stabilising the RH.

Oddy-type tests of a fresh saturated magnesium nitrate solution detected no corrosion<sup>22</sup>. However, tests of saturated solutions cannot be performed at 100% RH, but only at the DRH at 60 °C (ca. 42.4%, extrapolated from Wexler<sup>23</sup>). Thermodynamic calculations<sup>24</sup> using the ACCENT online calculator (<http://www.aim.env.uea.ac.uk/aim/accnt4/model.php>) yielded 0.17 ppb nitric acid (HNO<sub>3</sub>) in air over a solution of 5 mol of salt/kg of water. This is an order of magnitude lower than the average indoor background of 3 ppb<sup>25</sup>; therefore, it is neglectable. Indoor levels (24 h average) in Southern California museums in 1991<sup>26</sup> varied between 0.3 and 10.4 ppb but might now be lower because of NO<sub>x</sub> reduction and active filtering (if applied). Some sensitive dyes will fade at such levels sooner or later<sup>27,28</sup>.

When magnesium nitrate solutions absorb acidic gases, the solutions become more acidic. In equilibrium, the trace concentration of undissociated nitric acid (HNO<sub>3</sub>) increases, and more traces of neutral HNO<sub>3</sub> molecules enter the air. There is apparently just one case in the literature where this happened (unintendedly): Sharma<sup>29</sup> discovered potassium nitrate crystals on sensitive model glasses with an unstable composition (high amount of flux: 23.5% w/w K<sub>2</sub>O and 3% Na<sub>2</sub>O, and only 2.5% CaO stabiliser) stored over magnesium nitrate for 3 months. She had added a drop of acetic acid (ca 1 mmol) to the atmosphere to achieve 1209 ppm (=1,209,000 ppb) for corrosion studies. Totally absorbed in her 50 mL salt solution, that amounts to 20 mmol/L acid. Acetic acid concentrations in the atmosphere of wooden display cases are in the range of some 100 µg/m<sup>3</sup><sup>27</sup>. If we assume a daily absorption of 120 µg (=2 µmol) in 1 L solution, it would need 10,000 days (approximately 27 years) to reach such a concentration. Considering that our exhibits are much more stable than such model glasses and using more than an order of magnitude as a safety margin, it appears to be safe to change the magnesium nitrate solutions after 1 year.

In addition to our practical humidity tests in display cases at the Veste Coburg Art Collections (D), an international round-robin test of the RH in display cases over magnesium nitrate solution was initiated in the summer of 2023 for a full annual cycle. A How-to 'Guide for Participants' (updated after the project) was supplied. Recruited by newsletters, conference announcements, and personal contacts, conservators from more than 60 international collections registered, 30 provided a formal report after 1 year, and data from a total of 80 test series were evaluated at the end. The aim was to regain experience in the handling of such solutions in many types of display cases and museums, different climate zones, and buildings. No problems with the creeping of salts over the rim of the containers occurred with half-filled polyethylene boxes and a climate that was not too dry. Containers were placed at the bottom of the cases, and no spillage was reported. As expected for tight cases, the RH inside remained mostly constant with neglectable deviations, independent of the outside, over a full year. After installing an appropriate amount of the saturated magnesium nitrate solution, no maintenance (opening the case and adding salt or water) was required. For display cases, with daily AERs above 1 or 2, a larger solution volume is advisable. In such cases, when of considerable height, an RH gradient of a few percent was observed between top and bottom. Although ISO 483 limits the use for scientific testing to chambers smaller than 200 L, no fans were used to avoid the need for an electrical supply and the formation of aerosols from the salt solutions. Forced airflow is only acceptable when the solutions are covered by a gas-permeable membrane. Membranes<sup>5</sup> might also be a good protection against spilling, but they slow down the exchange of water molecules between the solution and air<sup>9</sup>.

The larger the solution surface (ideal: use most of the bottom area), the faster the humidity exchange, and the faster the desired RH is achieved after the case is closed. If rare openings are restricted to days when the RH in the room is close to that in the case, there is no need to add silica gel for fast (de-)



humidification in the display case ('tandem climatization')<sup>30</sup>. If potential acid emitters (e.g. oakwood) are present inside, the solutions should be changed regularly (see above).

Because of their positive experiences, 87% of the participants will recommend solutions to colleagues and continue to use them in their collections.

The use of a saturated magnesium nitrate solution in display cases allows to achieve two goals at the same time: constant RH at an ideal value for mixed collections containing organic materials and the absorption of corrosive pollutants in one. In the 2-year project, we proved that the solution has a long service interval of a full year; future research will explore that in more detail. Used solutions can either be directly used as garden fertiliser or larger amounts can be re-purified by the manufacturer.

As a precaution, large amounts of objects prone to acidic emissions, such as cellulose acetate or wood or materials highly sensitive to nitric acid, such as natural dyes, should not be displayed over magnesium nitrate.

If a lower RH is desired (e.g. for glass and metals), potassium carbonate (DRH = 43.2% at 15–30 °C), which is an alkaline solution, performs excellently in our tests<sup>21</sup>, and is recommended. For 'sick' glasses, magnesium chloride (DRH = 33.1% at 20 °C) has been used successfully over three decades at Veste Coburg<sup>30</sup>.

In contrast to active HVAC systems, passive methods satisfy the contemporary demand for sustainability: low maintenance effort, no permanent electricity consumption, no power supply, and no expensive equipment. The method is failsafe, as it does not rely on a working electricity supply, which is important for any museum's risk assessment.

A healthier atmosphere in display cases and energy savings: saturated salt solutions certainly deserve a revival!

## Data availability

Gas measurements are archived at Saarland University and available on reasonable request. The datasets generated during the round robin test are not publicly available due to privacy restrictions by the participants but are available from the corresponding author on reasonable request.

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## Author contributions

G.E. and C.B. conceptualised the project and wrote the grant application. K.F.S. and H.G. tested salt solutions in display cases at Veste Coburg. K.F.S. coordinated and evaluated the round robin test. R.P. and O.B. performed the gas measurements, O.B. curated and analysed the data, supervised by C.B., who also managed the project. G.E. coordinated it and wrote the draft. All authors read and approved the final manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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