

A comparison of diffusion tube determinations of formic and acetic acid concentrations in air

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Abstract

After inconsistent results of air concentration measurements of volatile organic acids in display cases at the Museum of London (UK) and in the City Museum of Kortrijk (Belgium), a comparison of methods was carried out amongst the institutions most actively involved in these determinations. Each laboratory had its samplers exposed to known air concentrations of formic and acetic acid in the calibrated exposure chamber at ICN and in three display cases at the City Museum of Kortrijk. After exposure the tubes were all returned to their origin and analysed. Comparison of the results shows that each laboratory is rather consistent but between laboratories numbers can differ with a factor 2.

Introduction

This comparison study was initiated at the previous IAQ meeting in Norwich when Halsberghe confronted various laboratories involved in air sampling and analysis with the inconsistency of their results. Earlier she had observed the formation of efflorescence on ceramics that had been exhibited several years in display cases of the City Museum in Kortrijk (Belgium) (fig. 1). Analysis of the crystals showed they contained mainly thecotrichite ($\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$), indicating the presence of acetic acid vapours inside the display cases. To confirm this observation she contacted the University of Antwerp, the University of Strathclyde and the Netherlands Institute for Cultural Heritage (ICN) with a request to measure the indoor air pollution levels inside the display cases. The three laboratories carried out their sampling and analysis independently, at different times during the year, under different conditions. The results showed very little consistency, but it was not clear what caused the large differences.

The three institutions decided to do this comparison study, in which also Oxford Brookes University participated. Since the comparison is not performed on the basis of a common Standard Operating Protocol and is not structured in accordance with official interlaboratory comparisons, this study should be regarded as a comparison 'pilot project'. Different sampling methods were applied under the same conditions followed by different analytical protocols to see how the results compare and to understand 'what the numbers mean'.

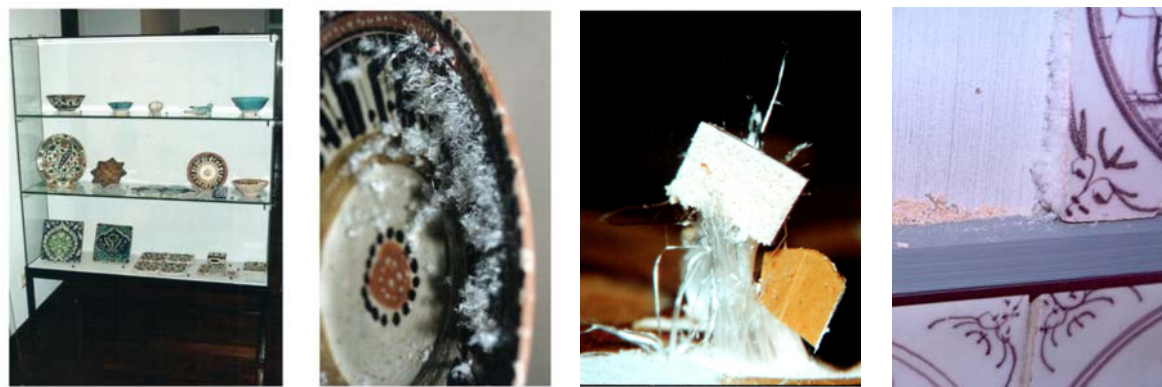


Figure 1. Nishapur display case City Museum of Kortrijk (far left) with efflorescence on ceramic plate (mid left); thecotrichite efflorescence destroying glaze of Flemish tile (mid right) and massive efflorescence growth (mainly thecotrichite and some halite) and result of damage in biblical tiles case (far right). Photos L. Halsberghe

Experimental set-up

The study was designed in two parts: 1) exposure of all samplers to known concentrations in the exposure chamber at ICN; 2) exposure of all samplers in the unknown environment of three display cases in the City Museum of Kortrijk. In both parts, the four laboratories prepared their own samplers and sent them to the exposure site, after exposure samplers were returned to their laboratory of origin for further analysis. All results were sent to ICN for interpretation. The concentrations of the exposure chamber were revealed only after analyses were performed.

The samplers used by the four laboratories are listed in table 1. Preparation and deployment of the samplers and the method of analysis are described elsewhere (van Bommel et al. 2001; Gibson et al. 1997; Kontozova et al. 2004a, 2004b). All laboratories calibrate their samplers with known solutions of acetic acid (HAc) and formic acid (HFor) and calculate the air concentrations from the amounts of acid trapped by the sampling reagent and the diffusion characteristics of the tubes (Fick's diffusion laws). For each deployment each laboratory provided four tubes.

Known concentrations of HAc and HFor in the exposure chamber were generated with permeation tubes as described earlier (van Bommel et al. 2001). It is important to realise that calibration of the vapour concentrations within the exposure chamber is based on weight loss of the permeation tube and determination of the air flow past the tube and in the chamber. Samplers were exposed for 1 week at 23°C and 50% RH. Air was mixed using a small computer fan. Earlier experiments have shown that the vapour concentrations inside the chamber are homogeneously distributed and Palmes tubes are not influenced by the air flow.

Table 1. Type of sampler and method of analysis of the participating laboratories

Laboratory	Type of sampler with reagent	Method of analysis
ICN	Palmes diffusion tube with KOH	Ion Chromatography
Strathclyde	Palmes diffusion tube with KOH	Ion Chromatography
Oxford Brookes	Palmes diffusion tube with KOH	Ion Chromatography
Antwerp	Radiello diffusion tube with TEA*	Ion Chromatography

TEA: triethanol amine

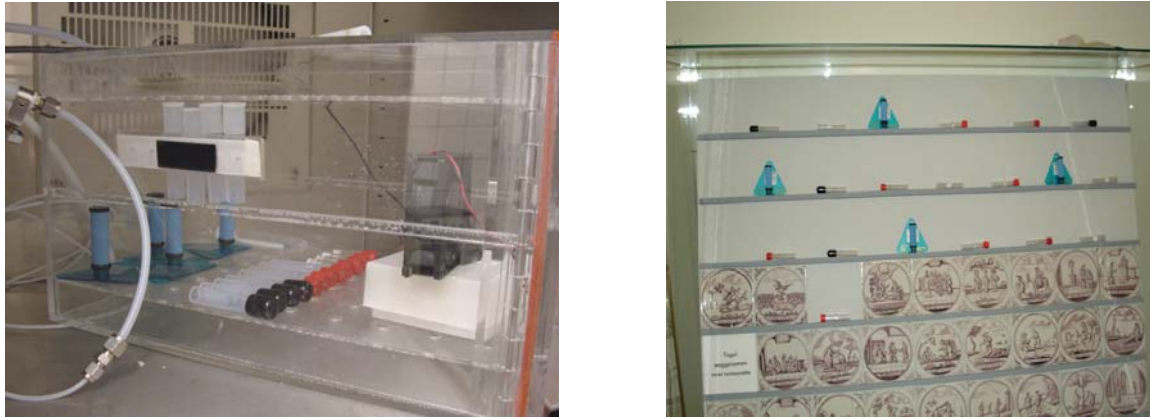


Figure 2. Deployment of sampling tubes in the exposure chamber at ICN (left) and in the Biblical tiles display case in the City Museum of Kortrijk (right).

At the City Museum of Kortrijk the samplers were deployed in the Nishapur display case, the Biblical tiles display case and a Porcelain display case. Again each laboratory provided four tubes for each case. The tubes were placed either in groups or spread throughout the case. Conditions in the Nishapur case were 22-26°C and 37-46% RH; in the Biblical tiles case 23-27°C and 50-55% RH.

Results and discussion

Looking at the results from the exposure chamber deployment (Fig. 3), the first observation is that the four laboratories have only a small spread in their individual results. They all operate rather consistently. Comparison of the determined concentrations with the calculated concentrations of HAc and HF or in the exposure chamber (purple and blue horizontal lines) shows pronounced differences. The results for formic acid show three laboratories within 12% of the calculated concentration. One laboratory is off by a factor of roughly 2. The results for

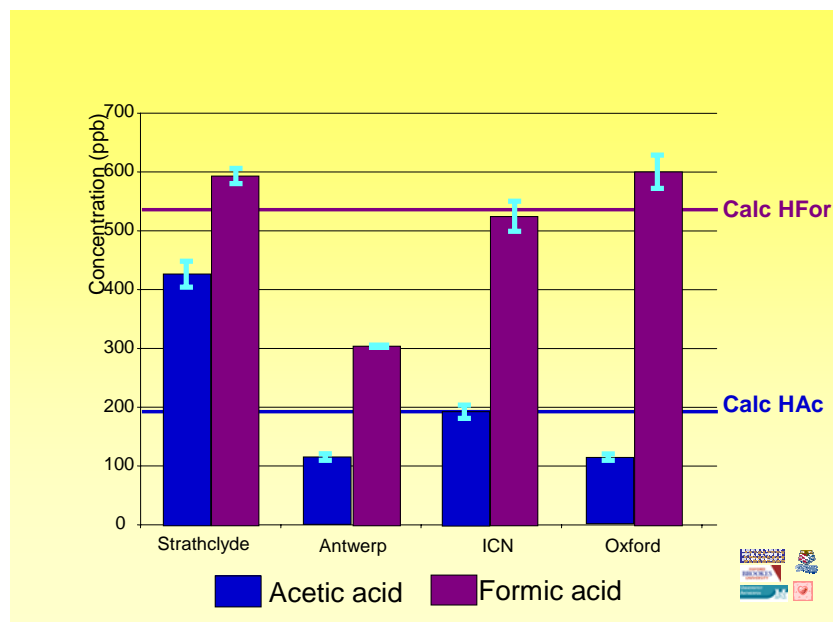


Figure 3. Results from the deployment in the exposure chamber to 194 ppb acetic acid (HAc) and 536 ppb formic acid (HFor).

acetic acid show bigger differences with two laboratories almost a factor 2 under the calculated value and one laboratory a factor 2 above. In both cases ICN is the most accurate, which may have to do with the fact that ICN did not have to transport tubes and could perform analysis immediately. Antwerp is consistent in determining half the calculated concentrations which is something that the laboratory will look into. The high acetic acid concentrations found by Strathclyde can be attributed to contamination while the low acetic acid concentrations determined by Oxford Brookes may be explained by the long time between exposure and actual analysis. Acetic acid is known to degrade over time whereas formic acid is rather stable.

When looking at the deployment in the display cases in Kortrijk, the results can not be compared with a known value, hence individual results are compared with the average. Figure 4 shows the results for acetic acid. In both the Nishapur and the Biblical tiles case ICN and Antwerp are closest to the average and show the same relative trends. The low concentrations measured by Oxford Brookes are in line with the low values found in the exposure chamber and may be contributed to the long time between deployment and analysis. Strathclyde is consistently too high which may be due to a contamination problem. All four laboratories are consistent in finding more acetic acid inside the display cases then outside.

In comparison with the results from the exposure chamber, Antwerp obtains relatively higher acetic acid results in the display cases. Indeed, ICN and Antwerp show almost identical results. A possible explanation for this could be an influence of air flow inside the exposure chamber after all. The Radiello adsorbing cartridges are covered by a micro-porous polyethylene tube, while the Palmes tubes are open at one end. Besides, this was the first time that Radiello samplers have been applied for the determination of organic acids.

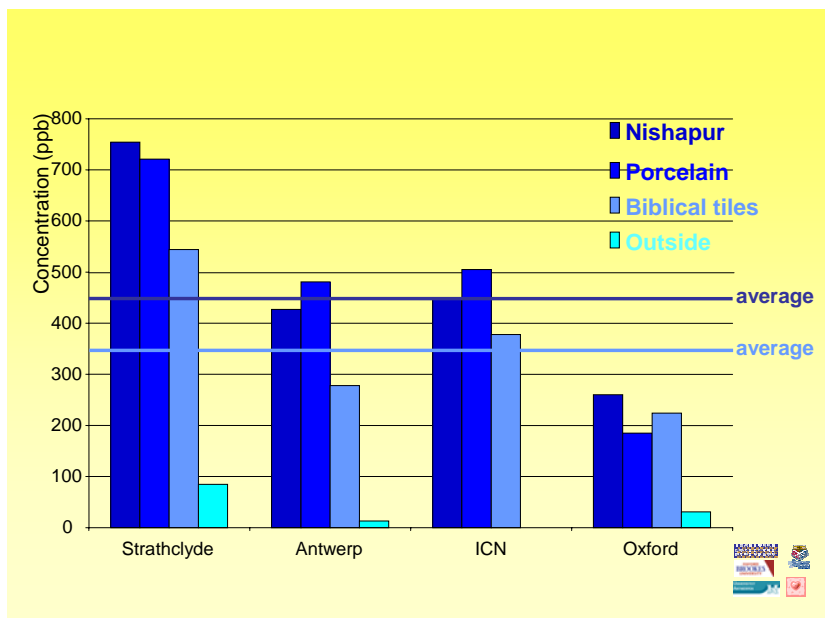


Figure 4. Acetic acid results from the deployment in the Nishapur (dark blue), Porcelain (blue) and Biblical tiles (light blue) and outside (turquoise) display cases in the City Museum in Kortrijk with horizontal lines indicating the average for the Nishapur (dark blue) and biblical tiles (light blue) cases.

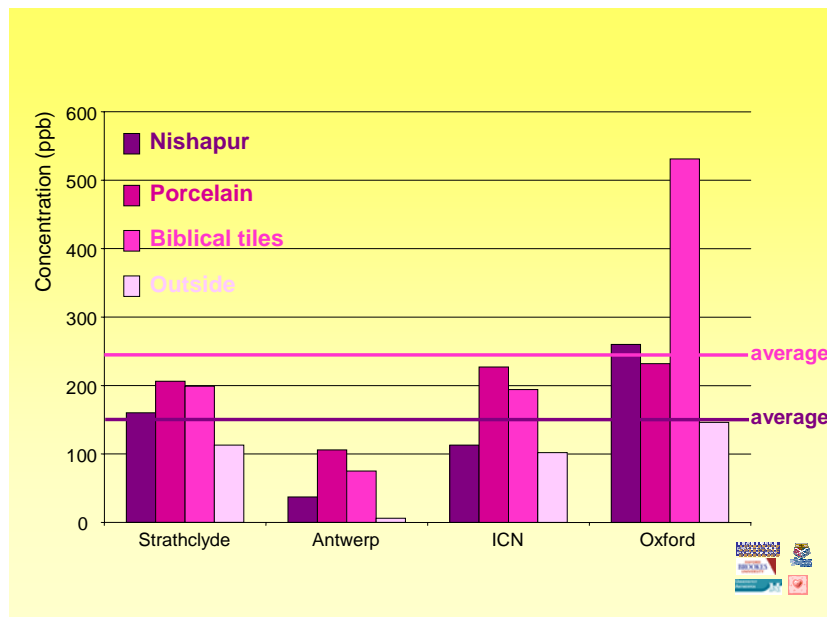


Figure 5. Formic acid results from the deployment in the Nishapur (dark purple), Porcelain (purple) and Biblical tiles (pink) and outside (light pink) display cases in the City Museum in Kortrijk with horizontal lines indicating the average for the Nishapur (dark purple) and biblical tiles (pink) cases.

Figure 5 shows the results for formic acid. Looking at the averages of the Nishapur and the Biblical tiles case, again two laboratories are closest to the average and show a similar pattern in values. However, now Antwerp is below the averages. Oxford Brookes is above the averages and shows a different pattern. Again all four laboratories are consistent in finding more formic acid inside the display cases than outside.

The results show that, at present, values of organic acid concentrations in air determined by different laboratories show considerable variation. From a pure analytical chemistry point of view these variations are large. However, looking at it from the perspective of conservation, the most important question is whether advice given, based on the analytical results, will differ greatly between the various institutes. All four laboratories will conclude that, since the acetic acid concentrations inside the cases are higher than outside, the source of acetic acid must be sought inside the display cases, probably the construction material. With the exception of Oxford Brookes (long time between sampling and analysis) all laboratories find higher acetic than formic acid concentrations. When the acetic acid concentrations in the three display cases are compared with the preservation target of 1 year or 10 years display without observable damage (Tétreault 2003), three of the four laboratories come to the conclusion that damage can be expected within approximately 1 year (Fig. 6). When asked whether the conditions inside the display cases meet a preservation target of 10 years, all four laboratories would conclude that they do not and that serious reduction measures are required to improve display conditions.

In reality at the City Museum of Kortrijk it took approximately 10-15 years before the efflorescence was noticed and alarm was raised, although a trained and focussed observer would have noticed damage at an earlier stage. One should keep in mind that there are additional factors that both accelerate and decelerate degradation. The ceramics contain salts, something Tétreault's preservation targets do not specifically take into account. There are also other pollutants present. Apart from the obvious formic acid, the museum suspects that the degrading PVC fabric in the cases emitted hydrochloric acid (HCl) gas which most probably

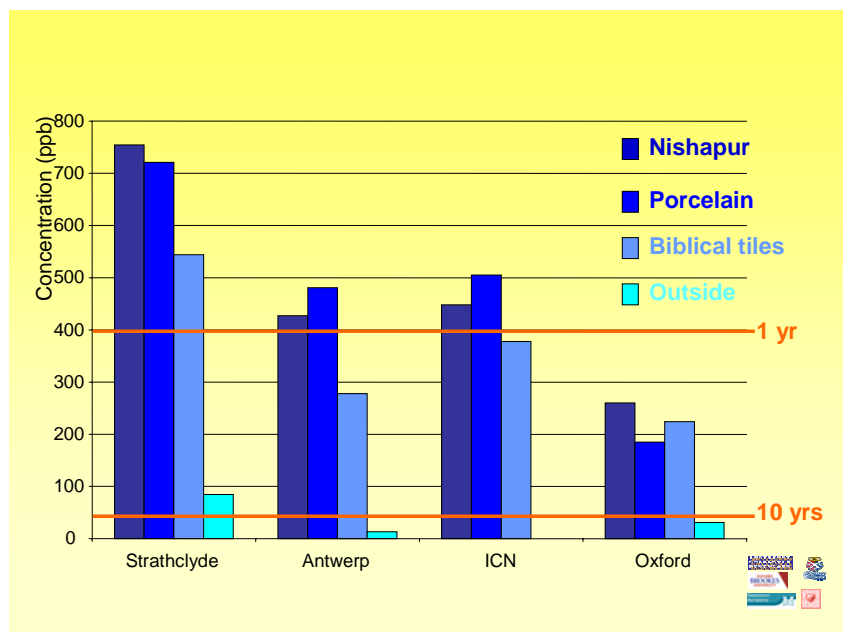


Figure 6. Acetic acid results from the deployment in the Nishapur (dark purple), Porcelain (purple) and Biblical tiles (pink) and outside (light pink) display cases in the City Museum in Kortrijk with orange horizontal lines indicating the preservation target for 1 year and 10 years no observable damage.

had an additional effect on the degradation of the ceramics. On the other hand, RH values have fluctuated and at lower levels they will have slowed down the formation of efflorescence. Altogether the analytical results and the interpretation in terms of conservation consequences are in line with reality. Both predictions based on the concentration levels and observations in reality indicate the occurrence of damage in a time span of 1-10 years.

Conclusion

Given the fact that this study is not an official interlaboratory comparison, the results are not as bad as they may look at first sight. Each laboratory provides consistent results with a precision (standard deviation divided by mean) in the range of 10-20%. Antwerp stays even under 10%. Also, each laboratory is consistent in the relative values. They find more organic acids inside the display cases than outside. Yet comparing the results of sampling and analysis from the different laboratories with each other, there are considerable variations. Values published in literature or provided in a report may well be twice as high or twice as low as stated. At first sight these variations are large, yet in the light of conservation consequences a factor 2 is not disastrous. Based on the results the conclusions and the advice for mitigation will be the same. These results once again stress that interpretation of analytical results requires knowledge, both about the procedures and their weaknesses and about the consequences for conservation. Now that the possible shortcomings in operating procedures have come to the surface, repetition of the study after improvements may give even better results.

Acknowledgements

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