Study on the off-gassing and storage environment in the conservation of Japanese woodblock prints

浮世絵の保存におけるオフガス特性とその収蔵環境に関する研究

ギマラエス ロメロ　アナ テレサ
Guimaraes Romero, Ana Teresa

1. Introduction

Organic acids – mainly acetic acid, formic acid – are among the many volatile organic compounds (VOCs) that are naturally off-gassed (emitted) from aging paper and wood objects, and their potential application as diagnostic tools to assess the conservation state of paper-based cultural property has been suggested before.[1,2] In addition, acetic acid has been singled out as specific degradation marker of acidified paper, as this VOC is often found present in comparatively higher concentrations in repositories containing paper-based collections.[3,4]

As such, this research began with the goal of measuring organic acids off-gassed from Japanese woodblock prints (*ukiyo-e*) as a potentially non-destructive way of accessing their state of acidification. Such method could've been employed as a preventive measure to detect ongoing acidification in woodblock prints, as well as other paper-based cultural properties, before visible signs of degradation appear.

However, as it will be demonstrated in the following chapters, no significant correlation was found between organic acid emissions and pH of prints. It was also observed that acetic acetic-concentrated storage spaces were not necessarily an indication of acidic/acidifying paper collections. Considering the findings gathered in this research, this dissertation theorizes that acetic acid is prone to accumulate inside closed spaces with low air-exchange rate due to its relative stability as an end-reaction product of hemicellulose decomposition.

This phenomenon is of particular importance to *ukiyo-e* collections. Accepted storage practices that protect the sensitive prints from damaging UV rays, humidity fluctuations, dust and pests, involve storing the prints in individual folders or semi-airtight storage boxes for prolonged periods of time. These practices may, conversely, aggravate the acidic off-gassing of woodblock prints and contributing to their acidification.

2. Measuring off-gassing: Preliminary testing at Hiroshige Museum of Art (Tendo, Yamagata)

The second chapter of this dissertation introduces the off-gassing measuring method used through this research and offers the first indications of storage influence in the prints' acidic off-gassing. A special apparatus made of acrylic sheets to firmly secure the print during measurement was built. Kitagawa™ precision gas detector tubes no. 910 for Organic Acids (acetic acid + formic acid) and no. 900NHH for Ammonia, mounted on ASP-1200 model air sampling pumps, were used to sample both acidic and alkali gaseous emissions. The first field experiment using this measuring method occurred in the Hiroshige Museum of Art in Tendo, Yamagata, where a woodblock print attributed to Toyokuni III & Hiroshige II that had been part of the museum collection for at least 50 years was measured for acidic off-gassing (Figure 1).

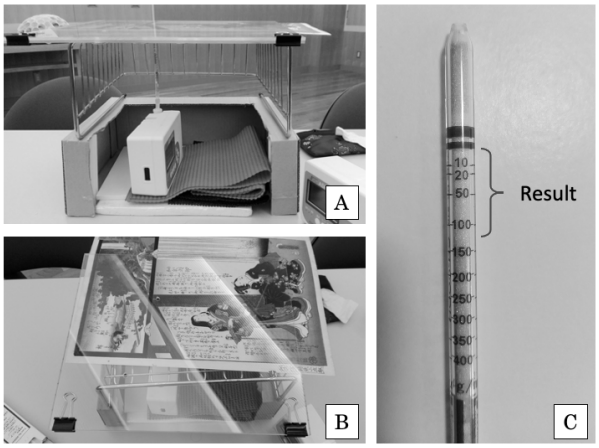

Figure 1. A and B: Outlook of off-gassing measuring method C: Detector tube after measurement.

When this measuring method was preliminarily tested in laboratory, different off-gassing values were collected

from different areas of the same print. However, the results obtained in the Hiroshige Museum were surprisingly homogenous. In addition, it was found that the print's organic acid off-gassing values were similar to the values of the folded Japanese paper that was enveloping the print in storage. Further investigation revealed that the museum's storage room had a considerable concentration of acetic acid in air compared to the other museum's rooms.

3. Correlation between off-gassing and acidification of woodblock prints

This chapter elaborates on the set of experiments that took place when the research goal was to hopefully find a linear correlation between off-gassing behavior and acidification, as well as the findings that redefined the research goal towards a direction that focused on the effect of the storage environment in organic acid accumulation inside containers with *ukiyo-e* collections.

Surface pH values and organic acid and ammonia gas emission concentrations were collected from six woodblock prints for a period of one year. Off-gassing measurements were performed with the same instruments as previously described, and mapping of surface pH values was done by agar gel pellet sampling method, based on the technique developed by researchers at the Smithsonian Institution.[5] Lastly, the environment inside the storage folders of each print was assessed for acidity using acid-detector (A-D) strips, developed by Image Permeance Institute.

Combined results from these experiments indicated an accumulation of acidic vapors inside storage folders. The folders with fewer openings had a stronger acidic environment inside. In addition, it was observed, after studying the acidification patterns of the prints, that the lesser acidified areas were located closer to openings in their storage folders. No significant correlation was found when organic acid off-gassing values were plotted against correspondent area pH values; however, moderate correlation was found when the former were plotted against change of pH value in a 3-4 month interval.

Finally, it was concluded that a varying percentage of measured organic acids emitting from the prints were of exogenous origin (room environment). The following chapter further explores the influence of environmental organic acids on the print's off-gassing.

4. The storage environment of woodblock prints – Influence in the acidic off-gassing of storage items (Part I)

A field experiment took place in the University of Tsukuba Library, with the goal of assessing how the storage environment was affecting the off-gassing of a selected *ukiyo-e* print from their collection.

The organic acid concentration in the Library's storage room and inside a wooden storage box housing a Meiji period ukiyo-e collection was measured, after which one print was selected for a VOC mitigation experience using a fan-filter unit (FFU). It was found that, despite the storage room concentration being within accepted thresholds of museum indoor pollution,[6] the organic acid concentration inside the storage box was three times higher the room's concentration.

The VOC mitigation experience which followed, consisted of sealing the selected *ukiyo-e* print with a small-sized FFU inside an Escal® plastic bag, so to create a closed, recirculating stream of clean air to rinse the print and eliminate its organic acid emissions (Figure 2). After being rinsed, the print was returned to its original storage place (inside the wooden box), and organic acid re-emission was measured after 20 days. The procedure was repeated, but in the second time, the rinsed print was put in a different storage place with clean air and organic acid re-emission was measured after 25 days.

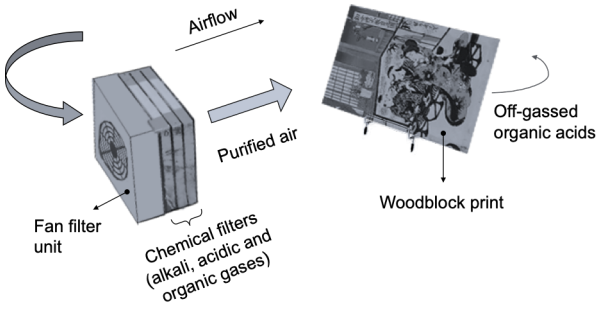

Figure 2. Design of the VOC mitigation experiment with an FFU.

Results from this experiment indicated that the wooden box storage was affecting the print's acidic off-gassing. It was found that, after the 20-day wooden box storage period, the print was emitting 32 ±19%. more organic acids compared to a 25-day storage period in a clean

environment. Results also revealed that off-gassing behavior was not uniform, as different areas of the print emitted different concentrations of organic acids, suggesting that pigments and/or relative location influenced off-gassing behavior.

5. The storage environment of woodblock prints – On the formation of microclimates inside storage boxes and mitigation strategies (Part II)

This chapter discusses a similar investigation and experiment as the previous chapter, this time focusing on the storage materials of an Edo period ukiyo-e collection, also housed in same storage room in the University of Tsukuba Library. Instead of a wooden box, the storage materials investigated here consisted of an acid-free cardboard archival box and a Japanese paper folder. The objective of this experiment was to gain a better understanding of the formation of these microclimates and evaluate the FFU system as mitigation strategy when employed on the storage materials.

The storage environment was first assessed for organic acid content, and once again, a similar organic acid-concentrated environment was found inside the archival box, with about 3 times the room's concentration. It was also found that the print in the middle of the stack was emitting more organic acids than the other measured prints. It has been suggested in published research that VOCs migrate between stacked sheets of paper until they become trapped in the middle of bottom sheets,[7] and data obtained from this experiment similarly hints at VOC accumulation happening in the middle prints.

The storage materials were then rinsed off organic acids by FFU system (as previously described), after which they were returned to their original positions in the storage room with the prints inside. For a follow-up period of 5 months, organic acid content inside the archival box and paper folder was measured.

Results from the follow-up measurement revealed an initial exponential rise in organic acid content inside the box that plateaued after roughly two months, for a short period, before rising again as ambient temperature rose with seasonal change (Figure 3). It was theorized that the rapid organic acid build-up inside a "clean" storage box made of allegedly low-emitting materials happened because of the semi-airtight construction of the box, which traps organic acids off-gassed from both prints and storage materials inside with nowhere to "escape", as the room's ventilation system does not reach to the interior of these boxes. It was also concluded from this experiment that the FFU system had a moderate success in mitigating organic acid concentrations inside the box even though it did not offer a permanent solution.

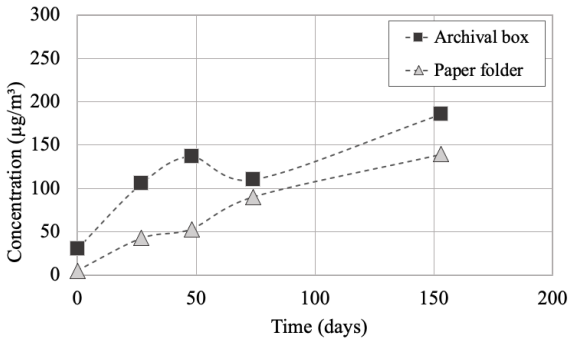

Figure 3. Re-emission of organic acids (μg/m^3) during the follow-up period.

6. Acidification of woodblock prints in an acetic acid-concentrated environment

A laboratory experiment aimed at observing the impact on pH and off-gassing in prints after exposure to an acetic acid-concentrated environment was developed and described in this chapter.

Samples representing common characteristics of *ukiyo-e* prints were prepared in laboratory, using non-bleached Japanese paper sized with an alum+*nikawa* solution and colored with pigments. Seven groups of samples were prepared: 1) unsized paper samples (A-Pa); 2) sized paper samples (B-Do); 3) sized paper samples w/ indigo (C-In); 4) sized paper samples w/ Prussian blue (D-Pr); 5) sized paper samples w/ orpiment (E-Or); 6) sized paper samples w/ red iron oxide (F-Re), 7) sized paper samples w/ red lead (G-Mi).

The samples were then exposed to 38 ppm, 3 ppm and 0 ppm acetic acid vapors in separate Pyrex desiccators. After a 14-day period of exposure, half of the samples were analyzed by ion chromatography (IC) (Metrohm Metrosep A Supp. 5-250/4.0 column combined with 3.2 mmol/L of Na_2CO_3 + 1mmol/L of $NaHCO_3$) for acetic acid adsorbed content. The other half was left to desorb excess gas for 7 days in a controlled environment, and then analyzed by IC to see retained acetic acid content

and calculate the off-gassed amount. Sample solutions prepared for IC analysis were also measured for pH.

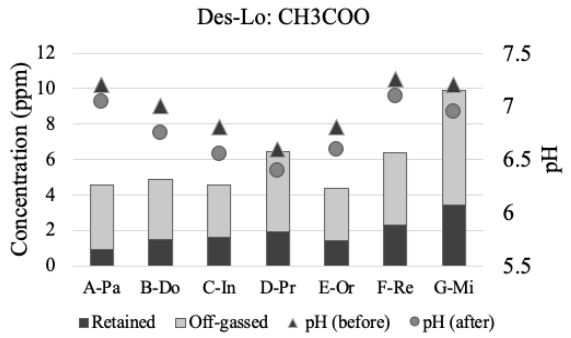

Figure 4. Retained and off-gassed conc. in samples, and pH value before and after exposure to 3 ppm vapors of acetic acid (Des-Lo).

Obtained results suggest that diverging off-gassing values in a multi-colored woodblock print may be attributed to different pigment characteristics, and it does not necessarily correlate to degree of acidification. It was also shown that exposure to acetic acid-concentrated environments contributed to heterogenous acidification of woodblock prints. However, severe acidification in certain samples was associated with excess oxalic acid formation induced by exposure to high concentrations of acetic acid that did not reflect normal storage conditions. As such, results from laboratory experiments should be interpreted carefully.

7. Conclusion

The research detailed in this dissertation showed that acidic off-gassing in woodblock prints is primarily indicative of their storage environment. The storage of woodblock prints in closed boxes of semi-airtight construction seemingly facilitates the creation of an organic acid-concentrated microclimate that may lead to VOC build up in center/inner areas of stored prints that are further away from the openings of a container, where more severe acidification may occur. Estimating the conservation risks of woodblock prints after long-term exposure to organic acid-concentrated microclimates in normal storage conditions is difficult as laboratory data is limited. It is, however, understood that some components of woodblock prints might make them some susceptible to organic acid-induced degradation, such as areas with pH-sensitive pigments. It was also understood that these prints tendentiously have a heterogenous pH distribution and areas with lower pH values would be more vulnerable to pronounced acidification in storage, which in turn, was found to moderately correlate to higher acidic off-gassing.

The findings compiled so far call for the re-evaluation of the use of storage boxes with semi-tight construction and for the development of mitigation strategies to combat VOC build up in storage microclimates. Using the FFU system for routine cleansing or, even employing traditional but forgotten practices like *mushiboshi* (periodical “airing” of stored artifacts) were suggested as simple and innocuous mitigation strategies. Future research should expand on these findings and examine the potential damage in collections associated with VOC-concentrated microclimates in storage containers, as well as explore practical solutions to combat this issue.

References

1) Strlič, Matija; Cigić, Irena K.; Kolar, Jana; De Bruin, Gerrit; Pihlar, Boris: *Non-Destructive Evaluation of Historical Paper Based on pH Estimation from VOC Emissions*, Sensors 7 (12), pp.3136-3145, 2007

2) Bembibre, Cecilia; Strlič, Matija: *Smell of heritage: A framework for the identification, analysis and archival of historic odours*, Heritage Science 5 (1), pp.1-11, 2018

3) Mašková, Ludmila; Smolík, Jiří; Ďurovič, Michal: *Characterization of indoor air quality in different archives – Possible implications for books and manuscripts.* Building and Environment 7, pp.59-70, 2010

4) Gibson, Lorraine T.; Ewlad-Ahmed, Abdunaser; Knight, Barry ; Horie, Velson; Mitchell, Gemma; Robertson, Claire J.: *Measurement of volatile organic compounds emitted in libraries and archives: an inferential indicator of paper decay?*, Chemistry Central Journal 6 (1), p.42, 2012

5) Hughes, Amy; Keynan, Daria: Testing the Waters: *New Technical Applications for the Cleaning of Acrylic Paint Films and Paper Supports,* The Book and Paper Group Annual, pp.43-51, 2013

6) Tokyo National Museum (ed): *Tōkyō Kokuritsu Hakubutsukan no Rinshō Hozon = Clinical Conservation at the Tokyo National Museum,* Bijutsu Shuppansha. 2013

7) Carter, Henry; Bégin, Paul; Grattan, David: *Migration of volatile compounds through stacked sheets of paper during accelerated ageing-part 1,* Restaurator 21 (2), pp.77-84, 2000