

VOC Testing for Books, Papers and Cellulose Acetate Laminated Documents

By Stephen C. Hobaica,
Supervisory Physical Scientist, Preservation Research and Testing Division,
Library of Congress, Washington, D.C.

This paper discusses planned research on volatile organic compounds (VOCs) off-gassing from paper, cellulose acetate laminated documents and other collection objects at the Library of Congress (LOC). The objective of this research is to 1) identify VOCs and their emission rate, 2) Identify specific VOC chemical markers that can be related to the physical condition of the paper and other materials in the book, 3) identify the chemical reactions that produce VOC markers and 4) characterize the material condition of the book's paper and other components (cover, ink adhesives etc.). This research begins at a fundamental level by measuring compounds being off-gassed from an internal research collection of generally well characterized books (Barrow Book collection) and mass deacidification control books and papers. The Barrow Book collection has over 900 books from the 15th to 19th century and was partially characterized by W.J. Barrow Research Laboratory¹ for tear resistance, pH, calcium carbonate content, alum, rosin, groundwood and fiber length. Other books that will be used are the LOC mass deacidification program's quality control books with twenty different types of paper without any printing ink. Other well characterized collections such as the British Library's Identical Book Project collection may also be investigated depending on availability.

The purpose of using these well-characterized books is to allow tracking of VOCs compounds being generated and relate the emissions to the physical condition of the books over an extended period of time. These naturally aged books offer two advantages. First there is no need for accelerated aging which may lead to erroneous predictions on the condition of the books (paper) and their expected lifetime. For example, a recent review indicated that accelerated aging based on the Arrhenius relationship does not allow for a reliable prediction of paper life expectancy.² Second, the information gained by the analysis is available to future investigators since the books will remain part of the collection and third, this collection can be shared with other investigators (e.g. British Library and others) to undertake a range of complimentary analyses.

VOCs being off-gassed are an important indicator of the condition of the book and paper. Books and papers are degraded by chemical reactions (hydrolysis and oxidation) and environmental activity (biological reactions, humidity³ and light). The reactions have been shown to off-gas a variety of compounds including acetic, formic and carboxylic acids, aldehydes, alcohols, aromatic and aliphatic hydrocarbons.^{4,5} Books are composite structures that absorb and deabsorb VOCs (such as pollutants) and VOCs produced from other objects such as building and collection housing materials. In addition, parts of the book may react differently and absorb VOCs at different rates and quantities. Each book is a composite of unique materials such as the cover (possibly parchment, leather, paper), paper (type and chemical composition), adhesive, inks, colorants and each of these materials may contribute to VOC emissions.

To separate out the paper emissions from these other materials, samples of different materials in the book may be taken and analyzed with the Agilent head space unit attached to a GC-MS. Once head space GC-MS analysis is complete a mass balance of VOCs in the books and air will be calculated to determine the VOCs from the paper. Another goal of the head space analysis also to yield information on other VOC markers for books (inks, adhesives, leather, vellum, colorants etc.). Studying the rate that paper absorbs VOCs (pollutants and from surrounding objects), environmental factors such as light and humidity³ will also assist in understanding their roles in VOC emissions from paper.

Specific VOC markers related to paper and cellulose degradation will be identified. A recent paper⁶ identified a relation between furfural with paper pH. Other VOC emissions such as toluene, vanillin, and formaldehyde were thought to have a statistical correlation with the carbonyl group in the cellulose structure.⁶ The rate of off-gassing in LOC experiments will be measured and characterized at room (68 to 72°F) and higher temperature conditions. LOC keeps many collections at room conditions and this information could be used with a future mobile mass spectrometer brought into collection spaces to measure VOCs in the space. Paper composition materials such as fibers, buffers (pH control), and degradation products (condition of the paper) will also be related to VOC emissions. VOC markers for other materials in books (inks, adhesives, leather, vellum, etc.) will be related to their physical condition.

The initial work with the Barrow Book collection will characterize pH of the paper, tear resistance, groundwood and fold endurance. These tests will be repeated along with molecular weight determination, elemental analysis⁷ by inductively coupled plasma optical emissions spectrometry (ICP-OES) or environmental scanning electron microscope (ESEM), water content of the paper, fiber analysis, fourier transform infrared (FTIR) spectra of the paper and tensile strength testing. Then the VOCs being off-gassed will be measured by multiple mass spectrometric and instrumental methods.

The specific instruments used will include but not be limited to the Agilent 5890N gas chromatograph, Jeol GC-mate, direct analysis in real time (DART) and Agilent 5975 quadrupole mass spectrometers and Agilent head-space sampling unit. Specific VOC markers will be related with the physical and chemical properties of the paper and cellulose acetate laminates (molecular weight, pH, chemical composition, and water content, fold endurance) for the purpose of determining the condition of the paper and what treatment is needed. The Agilent 5890N/5975 GC-MS can be used both for routine testing as well as research. The DART MS can be used to directly analyze solids (such as paper) at room and elevated temperatures and the Jeol GC-Mate can be used to not only measure compounds being off-gassed but also the breakdown these compounds further to better characterize their structures (MS-MS). Other goals of this research are to develop a reliable and repeatable methodology to study VOC emissions and the condition of the books and will include cellulose acetate laminated documents⁸ and work to study VOC emissions from housing materials.

This research will also serve to build a data base of compounds that are present in books and paper with each of the three mass spectrometers. This work is presently underway with the DART MS that characterizes volatiles, semi-volatiles from paper directly (without taking an air sample) and will continue with the Jeol GC-Mate mass spectrometer. For example DART MS work is characterizing 15 papers from the

ASTM's 100 year Paper Aging research project.⁹ This information will be part of the repository of reference samples to build upon for future work and made available to other VOC investigators. The repository will have specific information related to the GC-MS spectra produced by each instrument for various papers as well as instrumental methods used in the analysis (oven temperatures, MS setting, GC conditions etc.).

In summary this research will measure the VOCs from collections of books, paper and cellulose acetate laminates and chemically characterize VOCs. VOC markers for other parts of the book (inks, adhesives, leather, and vellum) will also be investigated. Specific chemical markers will be identified and related to cellulose degradation, the condition of the book and the chemistry of these markers will be studied. This work will begin to build a repository of VOC information with physical samples, spectrometric information and experimental methods.

References

1. "Permanence/Durability of the Book, volume VII, Physical and Chemical Properties of Book Papers, 1507-1949", *W.J. Barrow Research Laboratory, Inc.*, **1974**, Richmond, VA.
2. P. Calvini and A. Gorassinin, "On the Rate of paper Degradation: Lessons Learned from the Past," *Restaurator*, **2006**, 27, p. 275-290
3. C. Shahani, F. Hengemihle and N. Weberg, "The Effect of Variations in Relative Humidity on the Accelerated Aging of Paper", *Historic Textile and Paper Materials II, American Chemical Society*, **1989**, 63-79.
4. A. Lattuati-Deieux, S. Bonnassies-Termes, B. Lavedrine, *J. Chromatography, Part A.*, **2004**, 1026, p. 9-18.
5. G. Buchbauer, L. Jirovetz, M. Wasicky and A. Nikiforov, "Research Note: On the Odor of Old Books", *Journal of Pulp and Paper Science*, **1985**, Vol. 21, No. 11, J398-399.
6. M. Strlic, I. Cigic, J. Kolar, G. de Bruin and T. Steemers, "The Role of Volatile Organic Compounds in Paper Degradation" *Durability of Paper and Writing 2, 2nd International Symposium and Workshop, Book of Abstracts*, Ljubljana, Slovenia, July 7-9, 2008, 28-29.
7. C. Stephens, T. Barrett, P. Whitmore, J. Wade, J. Mazurek and M. Schilling, "Composition and Condition of Naturally Aged Papers", *Journal of The American Institute for Conservation*, **2008**, Vol. 47, No. 3, 201-215,
8. M. Ormsby, "Analysis of Laminated Documents Using Solid-Phase Microextraction" *Journal of the American Institute of Conservation*, **2005**, Vol. 44, No. 1, 13-26.

9. ASTM's paper Aging Research Program, Research Report (RR#) D06-1006:
ASTM International; West Conshohocken, PA. 2002.