Volatile organic compound testing for books, papers and cellulose acetate laminated documents

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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 (LC). 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) characterise 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-characterised books (Barrow Books Collection) and mass deacidification control books and papers. The Barrow Books Collection has over 900 books from the 15th to 19th centuries and was partially characterised by W.J. Barrow Research Laboratory (W.J. Barrow Research Laboratory 1974) for tear resistance, pH, calcium carbonate content, alum, rosin, ground wood and fibre length. Other books that will be used are the LC mass deacidification programme's quality control books with twenty different types of paper without any printing ink. Other well-characterised collections such as the British Library's (BL) Identical Book Project collection may also be investigated, depending on availability.

The purpose of using these well-characterised books is to allow tracking of VOCs 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 ageing, 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 ageing based on the Arrhenius relationship does not allow for a reliable prediction of paper life expectancy (Calvini & Gorassinin 2006). 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. BL and others) to undertake a range of complementary 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, humidity– Shahani *et al.* 1989 – 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 (Lattuati-Deieux *et al.* 2004; Buchbauer *et al.* 1995). 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 or paper), paper (type and chemical composition), adhesive, inks and colorants, and each of these materials may contribute to VOC emissions.

To separate the paper emissions from these other materials, samples of different materials in the book may be taken and analysed 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 is to yield information

on other VOC markers for books (inks, adhesives, leather, vellum, colorants, etc.). Studying the rate at which paper absorbs VOCs (pollutants and from surrounding objects), environmental factors such as light and humidity (Shahani *et al.* 1989) 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 paper identified a relationship between furfural and 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 (Strlič *et al.* 2008). The rate of off-gassing in LC experiments will be measured and characterised at room (68–72 °F) and higher temperature conditions. LC 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 fibres, 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 Books Collection will characterise pH of the paper, tear resistance, ground wood and fold endurance. These tests will be repeated along with molecular weight determination, elemental analysis (Stephens *et al.* 2008), by inductively coupled plasma optical emissions spectrometry (ICP-OES) or environmental scanning electron microscope (ESEM), water content of the paper, fibre analysis, Fourier transform infra-red (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), Agilent 5975 quadrupole mass spectrometers and Agilent head-space sampling unit. Specific VOC markers will be related to 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 for routine testing as well as research. The DART MS can be used to analyse solids (such as paper) directly at room and elevated temperatures and the Jeol GC-Mate can be used not only to measure compounds being off-gassed but also the breakdown these compounds further to characterise their structures (MS-MS) better. 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 documents (Ormsby 2005) and work to study VOC emissions from housing materials.

This research will also serve to build a database 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 characterises volatiles and 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 characterising fifteen papers from the ASTM's 100-year paper ageing research project (ASTM's Paper Aging Research Program 2002). 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 characterise 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, and 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.

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