RESEARCH PROFILE

On the Smell of Old Books

Leaf through an old book and one of the first things you'll notice is a distinctive musty odor—the product of volatile and semivolatile organic compounds (VOCs) from paper seeping into the air. This familiar scent speaks volumes about a book's condition. As a book ages, the composition of its VOC emissions changes characteristically.

In a recent *AC* paper (**2009**, DOI 10.1021/ac9016049), Matija Strlič and colleagues from University College London, the Tate art museum (U.K.), the University of Ljubljana, and Morana RTD (both in Slovenia) introduce a new method for linking a book's physical state to its corresponding VOC emissions pattern. The goal is to "diagnose" decomposing historical documents noninvasively as a step toward protecting them. "Ordinarily, traditional analytical methods like [LC] are used to test paper samples that have been ripped out," Strlič says. "The advantage of our method is that it's nondestructive."

Strlič calls the method "material degradomics". Like other —omic methods in research, he explains, material degradomics correlates phenotype—i.e., a book's condition—to metabolic byproducts: in this case, VOC emissions from degrading paper.

The team analyzed 72 well-characterized historical papers from the 19th and 20th centuries. These documents included papers made with rosin (a pine tar resin), bleached pulp, groundweed, and rag fiber. VOCs from these papers were measured using GC/MS. The 15 most abundant VOCs were then related statistically to key constituents in paper, including lignin, reducing carbonyl content, rosin, ash, pH, degree of polymerization, and protein content. The scientists used partial least squares (PLS) multivariate regression models to relate VOC peaks to their underlying chemical sources in paper, Strlič says. The team took this approach because different chemical constituents can emit the same VOCs, he explains. PLS is better suited to co-correlated data than classical regression models, which resolve more independent data sets.

ISTOCKPHOTO

Volatile compounds that account for an old book's smell also supply clues to its condition.

From a degradation standpoint, the two most problematic constituents in paper are lignin and rosin, Strlič explains. Lignin—a natural component in wood fiber, which replaced the more durable rag paper made before 1850—yellows with age. And rosin, which is a hydrophobic compound added to paper to make it suitable for writing, eventually breaks down into corrosive, acidic byproducts. As these two constituents degrade, they emit characteristic patterns of VOC emissions at predictive levels, Strlič and his colleagues found. Lignin releases acetic acid, hexanol, and furfural, whereas rosin gives off various aldehydes and ketones, in addition to 2-ethylhexanol. Some constituents—notably ash and protein content—could not be correlated with any VOC emissions.

Strlič hopes material degradomics methods will one day be used to evaluate culturally significant, historical papers. Ideally, a hand-held analytical device could "sniff" valuable holdings on a book-by-book basis, he says. Gerrit de Bruin, head of conservation at the National Archives in the Hague (The Netherlands), agrees. "We need more nondestructive tools for cultural forensics," he says. "As an end-user of this technology, I find the concept promising."

De Bruin and other specialists in the field worry especially about books, newspapers, and other documents made from 1850 to 1990. Paper products made during this period were "sized", or saturated, with rosin precipitated into fiber. The acidic byproducts released by rosin cause paper to degrade nearly 10× faster than earlier papers, which were sized with gelatin, a more neutral additive, Strlič explains. In the U.S. and elsewhere, rosin sizing was phased out for environmental reasons (rosin-containing pulp and paper effluents are toxic) and because the U.S. Permanent Paper Law, passed in 1990, gave paper mills incentives to convert to more alkaline processes. Meanwhile, papers made from 1850 to 1990 could degrade within one to two centuries after their production, posing a crisis for archives around the world.

According to Strlič, archives can slow degradation by decreasing temperature and relative humidity. Moreover, rapidly degrading documents can be neutralized in large reactors, he adds. The challenge is to quickly identify at-risk documents, says Cecily Grzywacs of the Getty Conservation Institute at the J. Paul Getty Trust in Los Angeles. "It's important that Strlič's team has introduced this degradomics approach," she says. "It provides a foundation to build on and opportunities for scientists to pursue and add more data. I hope someone does the same for other types of cultural objects."

—Charles W. Schmidt

10.1021/AC902143Z
Published on Web 10/01/2009