Material Degradomics: On the Smell of Old Books

7 **AUTHORS**, INCLUDING:

Irena Kralj Cigić
University of Ljubljana
23 PUBLICATIONS **293** CITATIONS

Jana Kolar
Morana RTD
91 PUBLICATIONS **1,567** CITATIONS

Material Degradomics: On the Smell of Old Books

Matija Strlič,[*,†] **Jacob Thomas,**[‡] **Tanja Trafela,**[§] **Linda Cséfalvayová,**[†] **Irena Kralj Cigić,**[§] **Jana Kolar,**[||] **and May Cassar**[†]

Centre for Sustainable Heritage, The Bartlett School of Graduate Studies, University College London, Gower Street (Torrington Place site), London, United Kingdom WCIE 6BT, Tate, Millbank, London, United Kingdom SW1P 4RG, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, Ljubljana, Slovenia SI-1000, and Morana RTD d.o.o., Oslica 1b, Ivančna Gorica, Slovenia SI-1295

We successfully transferred and applied -omics concepts to the study of material degradation, in particular historic paper. The main volatile degradation products of paper, constituting the particular "smell of old books", were determined using headspace analysis after a 24 h predegradation procedure. Using supervised and unsupervised methods of multivariate data analysis, we were able to quantitatively correlate volatile degradation products with properties important for the preservation of historic paper: rosin, lignin and carbonyl group content, degree of polymerization of cellulose, and paper acidity. On the basis of volatile degradic footprinting, we identified degradation markers for rosin and lignin in paper and investigated their effect on degradation. Apart from the known volatile paper degradation products acetic acid and furfural, we also put forward a number of other compounds of potential interest, most notably lipid peroxidation products. The nondestructive approach can be used for rapid identification of degraded historic objects on the basis of the volatile degradation products emitted by degrading paper.

The aroma of an old book is familiar to every user of a traditional library. A combination of grassy notes with a tang of acids and a hint of vanilla over an underlying mustiness, this unmistakable smell is as much part of the book as its contents. It is a result of the several hundred identified volatile and semivolatile organic compounds (VOCs) off-gassing from paper and the object in general.[1,2] The particular blend of compounds is a result of a network of degradation pathways and is dependent on the original composition of the object including paper substrate, applied media, and binding (the sum of its "biography" including possible interventions and its past and present local environment).

Recently, there has been an increased interest in the "smell of old books" and in VOCs emitted from historic paper in general.[2−5] The food and pharmaceuticals packaging industries have studied the transfer of taint and odor from paper and cardboard packaging during shipping and storage, extensively.[6,7] Other studies have developed VOC screening methods to identify the fraction of recycled pulp in board stock,[8,9] and identification of volatiles is now an almost routine analytical challenge. However, heritage institutions (libraries, archives, and museums) are interested in quantitative VOC analysis as a rapid diagnostic tool for the degradation and condition of their collections as well as evaluation of conservation treatments and materials analysis. Can we identify degraded books by their smell or even extract information about why the books degraded?

This question is especially interesting as heritage objects present particular problems for analysis either due to their uniqueness or due to diverging histories. Another factor is that it is often impossible to sample. This necessitates nondestructive/noninvasive methods, and headspace sampling coupled to GC/MS is especially appropriate.

The uniqueness and complexity, as well as limitations of destructive sampling, have limited much of heritage research to single object technical/material studies or to the degradation of constituent materials and/or simple surrogate objects. Yet models based on simple systems fall short of describing the complexity of heritage objects, and single object studies do not answer larger questions about classes of objects. The complexity of heritage objects is to an extent comparable to the complexity of living organisms. "-Omics" type methodologies have been developed for the study of living organisms,[10] could these methodologies be transferred to the study of heritage objects?

In this regard, the concepts of metabolomics[11−14] are most applicable to the purposes of heritage science. Metabolism, as a process in living organisms that have the power to adapt and renew, could be seen in parallel with degradation if one treats

* To whom correspondence should be addressed. E-mail: m.strlic@ucl.ac.uk.
† University College London.
‡ Tate.
§ University of Ljubljana.
|| Morana RTD d.o.o.
(1) Donetzhuber, A; Johansson, B.; Johansson, K.; Lovgren, M.; Sarin, E. *Nord. Pulp Pap. Res. J.* **1999**, *14* (1), 48–60.
(2) Lattuati-Derieux, A.; Bonnassies-Termes, S.; Lavédrine, B. *J. Chromatogr., A* **2004**, *1026*, 9–18.
(3) Strlič, M.; Kralj Cigić, I.; Kolar, J.; de Bruin, G.; Pihlar, B. *Sensors* **2007**, *7*, 3136–3145.
(4) Lattuati-Derieux, A.; Bonnassies-Termes, S.; Lavédrine, B. *J. Cult. Herit.* **2006**, *7*, 123–133.
(5) Gibson, L. T.; Robertson, C. *Advances in Paper Conservation Research Conference*, March 23−24, 2009, British Library: London, 2009, pp 40−42.
(6) Isinay, E.; Yüzay, S.; Pack, S. *Technol. Sci.* **2007**, *20* (2), 99–112.
(7) Forsgren, G.; Frisell, H.; Ericsson, B. *Nord. Pulp Pap. Res. J.* **1999**, *14* (1), 5–16.
(8) Ziegleder, G. *Packag. Technol. Sci.* **2001**, *14* (4), 131–136.
(9) Asensio, E.; Nerin, C. *Packag. Technol. Sci.* **2009**, *22* (6), 311–322.
(10) Goodacre, R; Roberts, L.; Ellis, D.; Thorogood, D.; Reader, S.; Ougham, H.; King, I. *Metabolomics* **2007**, *3* (4), 489–501.

Table 1. Definitions of Material Degradomics Terms

material degradomics	the analysis, both quantitative and qualitative, of the degradation products produced by a material, their dynamics, composition, interactions, and variations due to composition, degradation processes, use, and environment
degradome	the sum of the products of the various degradation reactions and their interactions
degradic profiling	quantitative analysis of a set of degradation products in a selected degradation pathway or a specific class of compounds for a particular object
degradic fingerprinting	unbiased, global screening to classify samples based on patterns of degradation products or "fingerprints" that change in response to degradation, use, storage conditions, or conservation interventions
degradic footprinting	fingerprinting analysis of degradation products in the microenvironment surrounding the material

Table 2. PLS Cross-Validation Data

measured property	range	cross validation	
		RMSECV	R^2
rosin	0−7 mg/g	1.2 mg/g	0.463
lignin	0−350 mg/g	75 mg/g	0.400
carbonyl group content	0−0.11 μmol/g	0.02 μmol/g	0.380
degree of polymerization	0−3000	580	0.352
pH	3.5−8.5	1.2	0.251

material objects as pseudo-organisms. Immediate parallels can be drawn between the degradome (the sum of the products of various degradation processes) and the metabolome of an organism. Through similarities with metabolomics,[15] we propose to define a new field of material degradomics (and related terms, Table 1). In the case of VOC analysis, the technique of footprinting[11,15] is especially applicable, as degradic footprinting samples the local environment of the object rather than the object itself. Other parallels can be sought between the genotype of an organism and historic recipes/procedures used to make a historic material/object. The phenotype of an organism, which results from expression of its genes and environmental factors, can be seen as analogous to the measurable or observable properties of a historic object. In this way, quasi-genotype−phenotype mapping experiments could be performed for heritage objects, either through systematically altering recipes (suppression, overexpression, knockout, etc.) and/or through experiments with altered environmental sequences to determine how these change the appearance and/or permanence of historically informed replicas.

The -omics approach, i.e., the data-driven holistic and inductive approach to experimentation replacing the hypothesis-driven, reductionist cycle of knowledge, has not been explored in relation to material characterization yet. The need for large sample sets (see, e.g., ASTM E1655−05) to generate a statistically significant sample space is undoubtedly a drawback of this approach. Material degradomics differs from other -omics-type research in that it is not possible to clone an object or grow new ones in a controlled environment. In relation to historic objects, it is often possible to collect expendable ones, and if the research question is related to variations in composition, it is possible to combinatorially prepare historically informed samples to study how small variations in composition affect the degradome.

In this work, we present a pilot study using well-characterized historic paper samples. The most abundant VOCs emitted from the samples were quantitatively determined using a footprinting method, and the resulting data were used to identify degradation markers for several types of paper commonly found in archival and library collections. The identified markers were then used to discriminate between papers of different stability. We investigated the properties important for the preservation of historic paper: ash, rosin, protein, lignin and carbonyl group content, degree of polymerization of cellulose, and paper acidity. While rosin and protein content provide information on the production technology, it is well-known that lignin-containing and particularly acidic papers are particularly unstable, which leads to a rapid decrease of the degree of polymerization and oxidation, resulting in a high content of carbonyl groups. In the present study, we were able to identify volatile markers, which could be applied to studies of actual books or documents to be used for monitoring degradation of a collection in real time, based on the off-gassed VOCs.

MATERIALS AND METHODS

Samples. We investigated 72 well-characterized 19th and 20th century historic papers from the SurveNIR reference sample collection.[16] The samples were selected on the basis of their composition to cover the span of important variability, i.e., the range of measured properties (Table 2). The sample set consisted of surface (gelatin) sized and rosin sized paper; bleached pulp, groundwood, and rag fiber containing papers; and coated and uncoated papers, representing the most important technologies of paper production. They were chemically characterized for lignin content and reducing carbonyl group content (using UV−vis spectrophotometry), rosin content (using LC-MS/MS), ash content (using dry ashing and gravimmetry), pH (using potentiometry), degree of polymerization (DP, using viscometry) and protein content (using HPLC). All methods have been described in a previous publication in detail.[17] Not all samples were analyzed for all properties: determination of DP using viscometry is not possible for papers with a high content of lignin while samples with rosin content were not analyzed for protein content, as papers were sized either using rosin or gelatin.

To characterize VOC emissions, we used a small amount of paper sample (10 mg) to avoid saturation of the solid phase

(11) Kell, D. B.; Brown, M.; Davey, H. M.; Dunn, W. B.; Spasic, I.; Oliver, S. G. *Nat. Rev. Microbiol.* **2005**, *3* (7), 557−565.

(12) Brown, M.; Dunn, W. B.; Ellis, D. I.; Goodacre, R.; Handl, J.; Knowles, J. D.; O'Hagan, S.; Spasić, I.; Kell, D. B. *Metabolomics* **2005**, *1* (1), 39−51.

(13) Hollywood, K.; Brison, D. R.; Goodacre, R. *Proteomics* **2006**, *6* (17), 4716−4723.

(14) Goodacre, R.; Vaidyanathan, S.; Dunn, W. B.; Harrigan, G. G.; Kell, D. B. *Trends Biotechnol.* **2004**, *22* (5), 245−252.

(15) Mapelli, V.; Olsson, L.; Nielsen, J. *Trends Biotechnol.* **2008**, *26* (9), 490−497.

(16) SurveNIR project webpage, www.science4heritage.org/survenir/ (accessed April 9, 2009).

(17) Trafela, T.; Strlič, M.; Kolar, J.; Lichtblau, D. A.; Anders, M.; Pucko Mencigar, D.; Pihlar, B. *Anal. Chem.* **2007**, *79*, 6319−6323.

microextraction (SPME) fiber, which could lead to distortion of the chemometric results. The sample was inserted into a 20 mL headspace vial and predegraded at 80 °C for 24 h. Subsequently, the resulting VOCs were extracted for 1 h at room temperature, using SPME fibers (Supelco, Bellefonte, PA) with a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) stationary phase and thickness of 50/30 μm, and the VOCs were then subjected to GC/MS analysis. As it is well-known and also recently demonstrated in the case of VOCs from paper,[4] the affinity of the SPME fibers toward various volatiles depends on their composition. For this reason, we opted for the most general one, i.e., DVB/CAR/PDMS.

GC/MS. An Agilent Technologies 7890A gas chromatograph, coupled to an Agilent Technologies 5975C quadrupole mass spectrometer equipped with a Gerstel cooled injection system CIS 4 was used at 250 °C. A 60 m Restek RTX-20 column, I.D. 0.25 mm and 1 μm stationary phase thickness (Restek, Bellefonte, PA) was used. The mobile phase used was helium (99.999%, Messer, Frankfurt, Germany) at a flow of ~0.9 mL min^{-1}. We used the following oven temperature program: 1 min at 40 °C, followed by heating to 280 °C at the rate of 10.0 °C min^{-1}, after which the temperature was constant for 40 min.

Ionization was performed using standard EI mode applying 70 eV at 230 °C. The interface was heated to 270 °C, and the quadrupole mass analyzer was heated to 150 °C. Manual integration of chromatographic peaks was performed in order to obtain best quality data. Peak identification was performed on the basis of comparison of mass spectra with the NIST library, and quantification was performed using peak areas in SIM mode. The 15 most abundant VOCs present in all chromatograms were selected for further analyses: acetic acid, benzaldehyde, 2,3-butanedione, butanol, decanal, 2,3-dihydrofuran, 2-ethylhexanol, furfural, hexadecane, hexanal, methoxyphenyloxime, nonanal, octanal, pentanal, and undecane.

Data Analysis. The peak areas were extracted, and a data table containing all peak areas and chemical information on the samples (pH, carbonyl group content, lignin content, protein content, degree of polymerization) was constructed.

Using partial least-squares regression (PLS), multivariate models that relate the VOC peak areas (measured variables) to the chemical parameters (quantifiable properties) of the samples were developed and validated using a leave-one-out cross-validation procedure. The optimal number of volatile compounds used for multivariate analyses was determined on the basis of the quality of PLS calibrations. Martens' uncertainty test was used to calculate the uncertainty of regression coefficients and to identify and eliminate variables (volatile compounds) that did not contain any relevant information.[18,19] For each model, the RMSECV (root mean square error of cross validation) was calculated and expressed in the same units as the original values in order to estimate the prediction capabilities of the models.[20]

As a method of unsupervised classification, principal component analysis (PCA) was used to summarize the main variations in variables and project them onto a few new principal components (PC). In order to prevent spurious correlations from being interpreted as meaningful information, leave-one-out cross validation was used to assess the model complexity. PLS and PCA multivariate calibrations were performed using Unscrambler v.9.7 (CAMO, Trondheim, Norway).

RESULTS AND DISCUSSION

Depending on the production technology and storage environment, paper can be a particularly durable organic material, its lifetime being measured in millennia.[21] However, most paper produced between 1850 and 1990 is likely not to survive more than a century or two due to the inherent acidity autocatalyzing its degradation. Cellulose is the most important structural element of paper, and it is well-known that the rate of its degradation depends on its immediate macromolecular and general environment. Historic paper can be an extremely diverse material: a number of production techniques and raw materials have been used throughout history.[22] Most of the research on paper degradation has so far focused on only a handful of different paper types. However, in order to holistically understand paper degradation, we have to take into account all parameters of paper composition and production.

The availability of a large number of samples, preferably historic samples, is a prerequisite for the degradomics approach. We used a well-characterized historic paper sample collection characterized for various properties: degree of polymerization of cellulose, lignin content, gelatin content, pH, aluminum content, ash content, fiber composition, rosin content, and reducing group content.[16]

PLS is of particular interest (Figure 1), as the loading weights express how the information in each measured variable, i.e., VOC, relates to the variation in the quantifiable property (Y), i.e., the chemical or physical property in question. The loading weights are normalized so that their weight can be interpreted as well as their direction. The measured variables with bigger loading weights are more important for the prediction of Y and, thus, represent suitable volatile degradation markers. A causal relationship (degradation pathway) should link the degradation marker with the property Y. In Table 2, the PLS calibration and validation data are provided, and in Figure 1, an example of the obtained PLS calibration and validation is given for rosin content in historic paper. The calibrations are of a relatively low quality due to the averaging effect of PLS; however, the predictions are still valuable as it is possible to extract qualitative data from the loading weight graphs, which enable us to interpret the effect that individual paper components have on its stability (Figure 1).

The loading weight graph for rosin content is particularly interesting. Rosin is 90% a mixture of related diterpene acids, mostly abietic and dehydroabietic acid, the other 10% being represented by "neutral substances", which are dominated by fatty acid esters and hydrocarbons formed from sterols.[23] The purpose of the addition of rosin was to make paper fibers hydrophobic in order to make sheets writable. Rosin sizing (as opposed to gelatin

(18) Martens, H.; Martens, M. *Food Qual. Prefer.* **2000**, *11*, 5–16.
(19) Martens, H.; Hoy, M.; Westad, F.; Folkenberg, B.; Martens, M. *Chemom. Intell. Lab. Syst.* **2001**, *58*, 151–170.
(20) Martens, H.; Naes, T. *Multivariate calibration*; John Wiley and Sons: New York, 1989.
(21) Strlič, M.; Kolar, J. *Ageing and stabilisation of paper*; National and University Library: Ljubljana, 2005.
(22) Hunter, D. *Papermaking: History and Technique of an Ancient Craft*; Dover Publishing: New York, 1987.
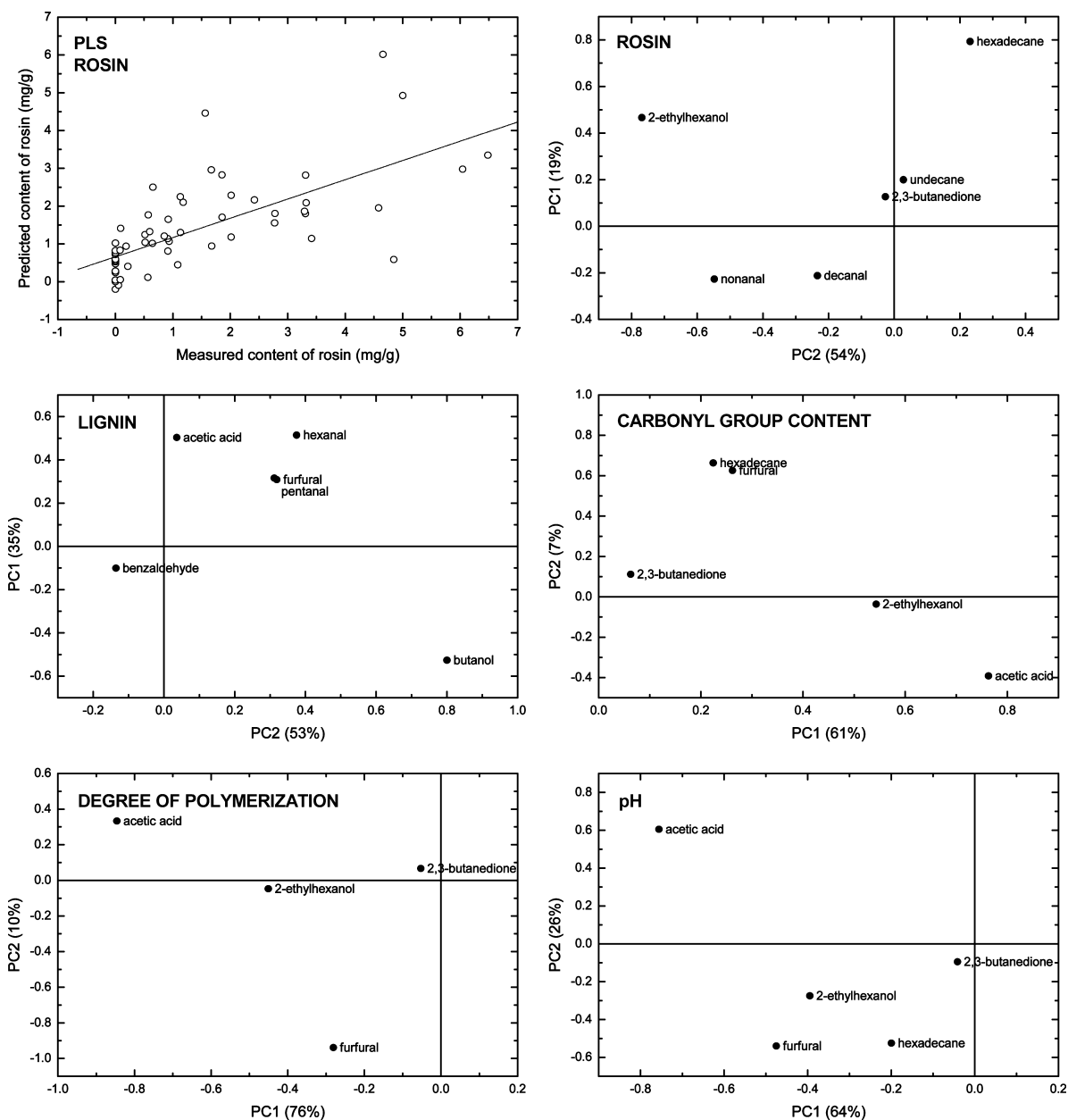(23) Roberts, J. C. *The Chemistry of Paper*; The Royal Society of Chemistry: Cambridge, U.K., 1996; pp 126–127.

Figure 1. (Top left) PLS cross validation for rosin content in paper on the basis of six volatile degradation products, with loading weights (top right). Other plots represent loading weight graphs for PLS calibrations for lignin and carbonyl group contents, degree of polymerization, and pH, as indicated.

sizing used in earlier papers) was used mainly after ~1850, and aluminum sulfate, used to precipitate rosin on fibers, is thought to be the source of acidity leading to low stability of rosin-sized papers. The volatile degradation compounds significant for prediction of rosin are various aldehydes, ketones, and 2-ethylhexanol. Aliphatic aldehydes and ketones are known to form during autoxidation of fatty acids[24] and are indicative of oxidative stress.[25] The main PC axis is PC2 and would seem to express polarity/nonpolarity.

Lignin is a complex aromatic cross-linked 3D polymer, and its content is of major interest in preservation of historic paper-based materials, as it has a pronounced effect on their stability.[26,27] It is well-known that furfural is a product of cellulose and hemicellulose degradation[28] in a series of reactions from acid-catalyzed hydrolysis of glycosidic bonds to dehydration of the resulting simple sugars. A higher acidity content of paper results in more abundant furfural formation, as recently shown.[3] Despite the number of VOCs off-gassing from lignin-containing food packaging materials,[1,29] the loading weight plot is dominated by acetic acid, hexanal, and also furfural, which demonstrate the high impact lignin has on the overall hydrolytic and thermooxidative instability of cellulose, in darkness.

(24) Spiteller, G.; Kern, W.; Spiteller, P. *J Chromatogr., A* **1999**, *843*, 29–98.
(25) Dalle-Donne, I.; Rossi, R.; Giustarini, D.; Milzani, A.; Colombo, R. *Clin. Chim. Acta* **2003**, *329*, 23–38.
(26) Bégin, P.; Deschâtelets, S.; Grattan, D.; Gurnagul, N.; Iraci, J.; Kaminska, E.; Woods, D.; Zou, X. *Restaurator* **1998**, *19* (3), 135–154.
(27) Jin, F.; Cao, J.; Zhou, Z.; Moriya, T.; Enomoto, H. *Chem. Lett.* **2004**, *33* (7), 910–911.
(28) Ziegleder, G. *Packag. Technol. Sci.* **1998**, *11* (5), 231–239.
(29) Nevell, T. P.; Zeronian, S. H. *Cellulose Chemistry and Its Applications*; Ellis Horwood: Chichester, 1985.
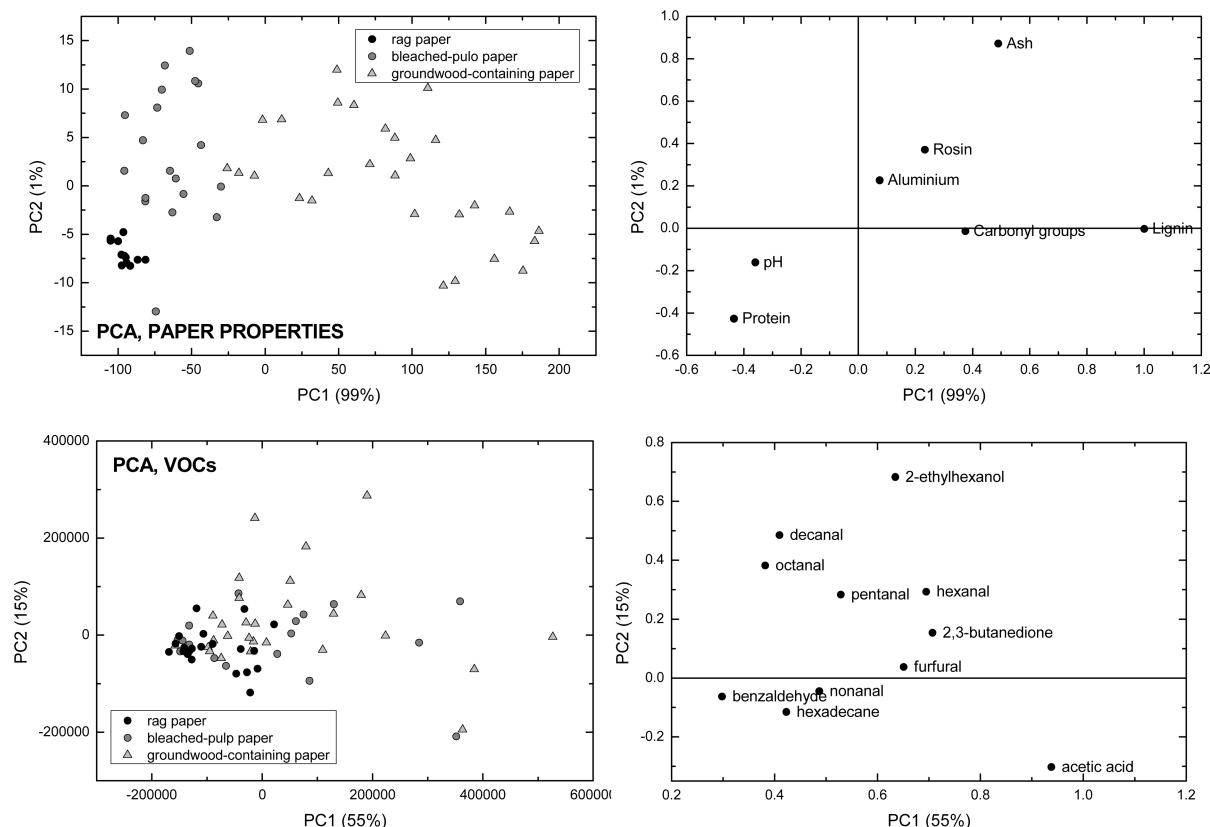
Figure 2. PCA (left) based on quantifiable paper properties: ash, rosin, protein, carbonyl group, and lignin contents, degree of polymerization, and pH (above) and volatile degradation products (below). Right: correlation loadings.

The loading weight plot for PLS of carbonyl content shows that an elevated content is a consequence of several factors: not only of degradation of the cellulosic components (furfural, acetic acid) but also of the rosin components (2-ethylhexanol and hexadecane). The content of rosin can, thus, be correlated with cellulose degradation, probably due to higher acidity, and therefore cross-correlated with the production of furfural, which is itself both a degradation product and a reducing aldehyde compound. It appears, however, that rosin content has a strong effect on accumulation of carbonyl groups.

DP is a parameter associated with the quality of cellulosic fibers and the extent of their degradation. However, considering that the initial DP values could have been very different, it is remarkable that a PLS correlation was obtained at all. Four compounds are negatively correlated with PC1, which represents the DP: acetic acid and furfural, which are cellulose/lignin degradation products, but also 2-ethylhexanol associated with rosin content. It is, thus, confirmed that rosin has a negative effect on the stability of paper.

Acidity of paper, measured as pH of its aqueous extract,[30] is both a measure of the accumulation of acids, because of degradation, and the result of acids introduced into the material during sizing. As it is the most important endogenous factor affecting the stability of historic paper, it is of interest if there are any volatile degradation products associated with it in order to provide the basis for a nondestructive method of determination. Recently, a study has shown[3] that furfural emission can be directly correlated

(30) Strlič, M.; Kolar, J.; Kočar, D.; Drnovšek, T.; Šelih, V. S.; Susič, R.; Pihlar, B. *e-Preserv. Sci.* **2004**, *1*, 35–47.

with paper acidity. Despite the less satisfactory PLS correlation, the loading weights show that acetic acid and furfural, but also compounds associated with rosin content (2-ethylhexanol and hexadecane), are associated with low pH. Acetic acid emission was previously not associated with pH directly,[3] probably because of its abundance in the headspace above degrading paper, which may lead to saturation of the SPME absorbent. In this work, the sample size was, therefore, adjusted, in order to be able to semiquantitatively evaluate the emissions of acetic acid, as well.

Not all measured properties were correlated with VOC emissions: for ash content and protein content, no meaningful PLS calibrations were obtained.

Historic paper is often classified according to the fibers used in papermaking: rag (usually linen, hemp, and cotton rags) containing paper, bleached pulp containing paper, and groundwood containing paper. The distinction between the groups is not very clear, especially because mixtures of raw materials were often used. Groundwood containing papers have a higher amount of lignin since the fibers have not been delignified. The vast majority of rag papers are hand-sized using gelatin, which is why protein content can be used to discriminate between rag papers and other classes. In Figure 2, the papers group into the three categories based on the quantifiable properties very well. The most valuable information can be extracted from the positions along the PC1 axis, which covers 99% of the total information: PC1 is dominated by lignin content and PC2 is dominated by ash and protein content. It is also evident that rag papers generally have higher pH than other papers used in the study, as pH is positively correlated with protein content. Carbonyl group content, which is associated with

oxidative degradation of organic paper components, is positively correlated with lignin and rosin content and negatively correlated with protein content. DP could not be used in this part of the study, as it cannot be determined for high lignin containing papers due to their insolubility in the solvent used for viscometry. Ash content is negatively correlated with protein content since fillers (which contribute to ash content) are mainly associated with modern papermaking. Rosin content also plays a role in the separation of rag papers from other papers, and it is anticorrelated with protein content, which is understandable, as papers were either rosin or gelatin sized. Aluminum, interestingly, does not play a major role, which is contrary to the popular belief that aluminum can be associated with paper acidity: it may have been immediately after papers had been sized, but not after decades of natural degradation.

Using VOCs, a different classification of the samples is achieved, which is of high interest. PC1 is dominated by acetic acid, a general degradation marker. PC2 is dominated by a variety of aldehydes and 2-ethylhexanol, which are associated with rosin content. Furfural, as a general degradation marker, affects only PC1. It appears that rag papers dominate a cluster of stable papers, while the rest fan out according to rosin and lignin content. Such separation could be the consequence of the fact that all the studied papers degrade according to the same mechanisms: acid catalyzed hydrolysis and oxidation simultaneously. Such classification is of considerably higher interest than the one on the basis of quantifiable properties, because it could lead to development of a method for classification of differently stable papers on the basis of VOC emission.

Using PLS, we have, thus, shown that 11 out of the 15 major volatile degradation products can be associated with a specific paper component and most are degradation markers. The PCA classification based on VOCs reveals further information on the difference in the effect of rosin and lignin on paper degradation, which should be studied in more detail. There also seems to be a significant difference between the amount and identity of volatiles emitted by historic degraded papers (as discussed in our study) and contemporary nondegraded paper samples (as discussed in the literature). We are focusing further research on increased sample throughput with suitable data pretreatment to increase the value and amount of extractable information based on the principles of degradomics.

While a destructive approach has been required in the development phase, we believe that this technique eventually can be used on individual paper documents or to survey large collections in a wholly nondestructive manner. Capture of VOCs in a sampling enclosure or in standing library stacks followed by degradomics data analysis could eventually be used to evaluate the type, present status of, and the future likely stability of paper-based historic documents.

CONCLUSIONS

We have successfully transferred the -omics concepts to the field of study of degradation of materials, paper in particular. Analyses of volatile degradation compounds formed during the degradation of a number of real historic samples were performed, and peak areas of the major compounds were compared with quantifiable paper properties using multivariate data analyses, i.e., partial least-squares and principal component analyses. This represents the first holistic and inductive approach to experimentation augmenting the overwhelming body of hypothesis-driven research in heritage science.

The approach allows us to understand the close relations between various paper components affecting paper degradation (rosin, lignin), the consequences thereof (content of carbonyl groups), and properties indicative of material condition (cellulose degree of polymerization, pH). We have shown that

(1) volatile degradic footprinting is a key tool to advance our understanding of the pathways leading to production of VOCs during paper degradation

(2) the composition of papers can be deducted on the basis of volatile degradation products

(3) VOCs, which generate the smell of books, provide information on paper condition and stability

Despite the drawbacks associated with the need for numerous samples, which can be prohibitive, our understanding of complex reaction systems leading to degradation of valuable heritage materials can be greatly increased using the proposed material degradomics approach. However, the approach is generally useful for all materials where degradation is an economic concern, e.g., polymers, food, and pharmaceuticals. A systematic variation of material composition (through production of historically informed replicas in the case of heritage objects) and degradation environments (under the influence of light, heat, oxygen) will not only inform stabilization strategies (e.g., using antioxidants, modified environments, or cool storage) but also could lead to optimization of production methods of materials themselves.