CMA4CH 2014, Mediterraneum Meeting
Employ the Multivariate Analysis and Chemometrics in Cultural Heritage and Environment Fields
5th ed., Rome, Italy, Europe, 14-17 December 2014

Multivariate Analysis of Pigments, and Detection of Environment and Treatment Changes on Historic Cartography, Manuscripts and Objects

F. G. France[1], M. Wilson[1], J. Hessler[2]
[1]Preservation Research and Testing Division, Library of Congress, U.S.A.
[2]Geography and Maps Division, Library of Congress, U.S.A.

Abstract

Multivariate and chemometric analysis of spectral imaging data can be used to non-invasively characterize colorants and pigments in historic documents and Pre-Columbian objects. Multivariate analysis of spectral image sets has detected changes due to exposure of cultural heritage documents and objects to various environmental conditions, including the assessment of changes during short-term exhibits of light-sensitive materials. Spectral imaging data analysed by multivariate analysis can also detect historic treatments of objects, and has been utilized effectively to non-invasively monitor the impact of modern treatments on historic cultural heritage materials, before changes are apparent in the visible region.

Introduction

The successful transfer of spectral imaging and analysis to cultural heritage institutions has led to applications that enable non-invasive chemical identification of historic materials, the recovery of obscured and degraded non-visible information, and the capacity to monitor non-visible changes in fragile materials to optimize conditions for storage and display. Spectral imaging analysis advances the capability for non-contact chemical characterization of colorants, inks, and substrates through their specific spectral response, aiding provenance of historic artefacts [1]. Monitoring deterioration or changes due to exhibit and other environmental conditions is critical for the longevity of cultural heritage objects. The ability to track changes and assess the impact and success of treatments with multivariate analysis ensures no unwanted effects from conservation actions intending to preserve and stabilize significant objects. Furthermore, analysis of spectral images has the added benefit of providing a spectral map locating each individual compound over the entire surface of the object, as opposed to the more common single-point analysis of many other chemical analytical techniques [2].

Materials & Methods

The Library of Congress (LC) conducts spectral imaging with a customized spectral imaging system, a 39 mega-pixel Monochrome E6 Camera with Kodak CCD sensor (7216 × 5412 pixel array with linear dimension of 6.8 microns), and integrated LED illumination panels containing 16-23 wavebands from the ultraviolet, visible and near infrared spectral regions (365nm–1050nm) developed to image a wide range of collection items. Remote sensing imaging spectroscopy has demonstrated that many features have absorption features 20-40 nm wide at full width half maximum (FWHM), enabling the spectral imaging system to acquire data for the direct identification of a wide gamut of organic and inorganic materials [3]. The data cube used for multivariate analysis incorporates the captured UV, visible, and NIR spectral images in reflected, transmitted, and raking (side-lighting) illumination orientations, with all images fully registered. This minimises handling of fragile items and offers potential for significant post-acquisition analysis. Multivariate analysis of the spectral image cube is performed using multiple analytical tools, including Principal and Independent Component and Least Squares Analyses (PCA, ICA, LSA) using Solo+MIA, ImageJ and ENVI software. Pre-processing of image data for chemometrics was critical to assure clear separation of spectral components within the data sets. The LC 1513 Ptolemy *Geographia* with 47 hand-coloured maps included 7 in poor condition, showing verdigris degradation and requiring stabilization and treatment. Verdigris offset onto opposing pages was causing further deterioration and obscured viewing of the maps. Multivariate analysis of spectral data was conducted with PCA and spectral curve analysis of images from before and after treatment, with chemometric calibration based on the reference colour standard used in the imaging. This analysis assured fluorescence had not increased due to a treatment to remove and reduce the verdigris offset, and confirmed no loss of a fugitive organic yellow colorant in the map border. Spectral imaging data-cubes were analysed to non-invasively confirm the identification of colorants on early nautical charts – Portolans, from 1320 (Mediterranean) and 1565 (Central and South America Pacific Coast). While these charts were usually used to depict travel in the Mediterranean, the 1565 was a very early chart probably created in South America. These fragile manuscripts could not be sampled, and chemometric analysis of spectral imaging data allowed researchers to characterize pigments and determine provenance of the artefacts. Mayan clay flasks from the late classic period (600-900 AD) that are part of the Kislak Collection at the Library were also examined to identify pigments and reveal any previous treatments.

Results

Multivariate analysis of the spectral imaging data from the Ptolemy Geographia indicated the success of applied treatments that removed the verdigris staining of adjacent pages, with the spectral response of the stained paper nearing the expected response of the non-stained paper, validating the successful application of the chosen treatment solution. Multivariate image analysis indicated no loss of the fugitive yellow border colorant. Analysis of Portolan chart data to characterize colorants revealed the use of a local indigenous pigment (indigo) on the 1565 chart, later over-painted with another blue pigment azurite, data only able to be separated through spectral analysis. Multivariate analysis of deteriorated provenance data from the toponyms (place-names) allowed confirmation of accurate dating for the 1320 chart. As illustrated in figure 1, assessment of the Mayan flask clearly revealed earlier repairs, most visible in the infrared region, suggesting a clay-type filler.

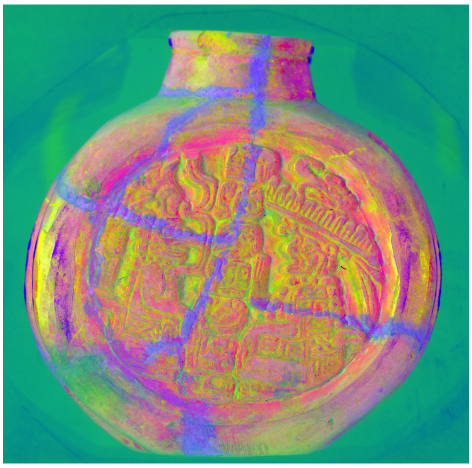

Figure 1: Principal Component Analysis (PCA) Pseudocolour Image - Prior Treatment

Conclusions

Multivariate analysis of spectral images of cultural heritage objects with PCA, ICA and LSA provides a powerful tool for non-invasive research linked with a range of complementary techniques. The chemometric linking of standardized data sets enables researchers to interpret results from a broader range of data, ensuring a multidisciplinary and collaborative approach to the preservation of cultural heritage objects. The capacity to assess the spatial distribution of materials greatly augments an objective understanding of the heritage material, allowing layers of scientific, cultural, technological, and historical information to be integrated and mapped. Assessing the impact of treatments and environment before any damage occurs can greatly increase the longevity of heritage materials.

References

1) F.G. France, M.B. Toth, Spectral Imaging for Revealing and Preserving World Cultural Heritage, Proceeding of *19th European Signal Processing Conference, EUSIPCO* (2011), 1450-1454.
2) F.G. France, Advanced Spectral Imaging for Non-invasive Microanalysis of Cultural Heritage Materials: Review of Application to Documents in the U.S. Library of Congress, *Appl. Spectrosc.*, 65(6), (2011), 565-574.
3) S.L. Ustin, D.A. Roberts, J.A. Gamon, G.P. Asner, R.O. Green, Using Imaging Spectroscopy to Study Ecosystem Processes and Properties, *Bioscience*, 54(6), (2004), 523-534.