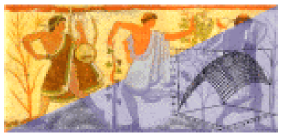

Monitoring of the Surface of Paper Samples Exposed to UV Light by ATR-FT-IR Spectroscopy and Multivariate Control Charts

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Abstract

The effect of the exposure of paper samples to UV rays was monitored through the use of ATR-FT-IR spectroscopy and multivariate statistical tools. Three types of paper were used in this study: common laser printer paper, sheets from a newspaper and sheets of light-sensitive fax paper. The samples were previously characterised through ATR-FT-IR spectroscopy to describe the natural experimental variability. Then, they were exposed to UV light for a total of 30 hours: the exposure effects were monitored through the same spectroscopic technique. Finally, multivariate statistical tools were applied to the final dataset, coupled to the construction of multivariate control charts, to identify the effects played by UV light on the samples surface.

Introduction

This contribution reports an application of multivariate statistical process control to the field of cultural heritage. The conservation state of the samples is treated as an industrial process and monitored by multivariate control charts. The method proposed has already been successfully applied to different substrates with good results [1-4]. It is here applied to paper samples exposed to UV light. The method exploits the principles of statistical process control, to identify possible damages on the surface of samples exposed to accelerating ageing conditions. A set of ATR-FT-IR spectra is collected for every type of sample (three different types of paper) to provide an initial description of the natural system variability (afterwards called characterisation analyses); then, the same spectroscopic technique is used to monitor the exposure of the different samples of paper to UV light (for a total exposure of 30 hours; afterwards called degradation analyses). The spectra collected for every type of paper (one separate dataset for each type of paper studied) are then treated by multivariate chemometric tools; the procedure involves a multi-step analysis:

- Baseline and smoothing;
- Principal Component Analysis (PCA) on the characterisation analyses, in order to extract the significant components and identify independent sources of information;
- Re-projection of the degradation analyses on the space given by the significant PCs;
- Construction of the Shewhart's multivariate control charts and Cusum charts for each significant component;
- Construction of the SMART chart (T^2 Hotelling and DModX) on the significant PCs.

Experimental

Three different types of paper were used: common white paper for laser printers, typical newspapers paper, light-sensitive fax paper. Three sheets of 2 x 8 cm for each type of paper were used, to provide three replicates of each spectroscopic analysis. 15 characterisation analyses were registered for the former two type of papers and 20 for the light-sensitive paper: each of them was replicated three times, one for each sheet of paper, providing a total of either 45 or 60 characterisation spectra.

After the characterisation phase, the samples were exposed to UV light (UV lamp emitting at 254 nm, 15 W) for a total of 30 hours. After each hour of exposure, one IR spectrum was registered for each sheet of the three types of paper, providing a total of 90 degradation spectra.

An AVATAR 370 FT-IR (Thermo Nicolet Corporation, USA) was used, equipped with a He-Ne laser emitting at 632.8 nm with a power of 50 mW. IR spectra were collected by the SMART accessory, pressing the sample over the Zn-Se crystal. All spectra were registered from 3750 to 650 cm-1, with a resolution of 4 cm-1 and 64 scans. The background was collected before each spectrum.

Statistical calculations were performed by Unscrambler 9.5 (Camo, Norway) and Excel 2000 (Microsoft Corporate, USA).

Results

A dataset for each type of paper analysed was built, including both characterisation and degradation analyses, with dimensions 135 x 1738 (135 being the spectra: 45 characterisation plus 90 degradation spectra or 150 x 1738 (for the fax paper); 1738 being the wavelengths. Each dataset was centred on the characterisation analyses. PCA was then performed on the characterisation analyses; two PCs were retained as significant for each dataset considered, accounting for about 96-99% of the total variance contained in each of the 3 datasets. The degradation analyses were then re-projected on the space given by the significant PCs identified. Shewhart, CUSUM and SMART charts were built for each significant PCs, for each dataset. Results are reported here for light-sensitive paper. Shewhart charts (fig1 top) show some points out of the control limits and a general decrease of the scores after during the UV treatment. Cusum charts however prove to be more effective in the identification of a damage on the surface (fig1 bottom), in fact they allow to point out the moment in which the UV treatment began, showing a linear negative trend after the first degradation analysis. The joint analysis of scores and loadings allowed the identification of the spectral regions responsible for the differences between characterisation and degradation analyses. The analysis pointed out a general decrease of the main peaks related to cellulose and other paper components showing thus a general degradation of the sample during the treatment. Similar conclusions could be driven for the other two types of paper, even if they are less sensitive to the degradation process applied.

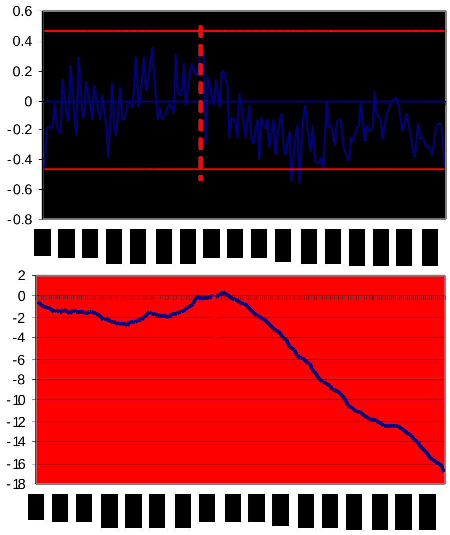

Figure1: Shewhart and CUSUM charts of PC_1 for light-sensitive

Conclusions

A method is proposed for the identification of possible damages caused to the surface of paper samples by the exposure to UV light, based on the coupling of spectroscopic techniques to multivariate process control principles. Multivariate control charts proved to be efficient in the monitoring of the process of exposure to UV light, in the identification of the exact moment in which an effect on the surface is detected and in pointing out the causes producing the damage effect.

References

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