SUPPLEMENTARY MATERIAL

Characterization of foxing stains in early 20th century photographic and paper materials

Aurora Modica^a, Maurizio Bruno^{a*}, Marco Di Bella^b, Maria Francesca Alberghina^c, Maria Brai^{c,d}, Dorotea Fontana^c, Luigi Tranchina^d

^a. *Department STEBICEF, University of Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy*

^b. *Corso di Laurea in Conservazione e Restauro dei Beni Culturali (PFP 5) – University of Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy*

^c. *Department of Physic and Chemistry, University of Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy*

^d. *Laboratorio di Fisica e Tecnologie Relative (FTeR), Sistema di Laboratori di Ateneo – UNINETLAB - University of Palermo, Viale delle Scienze, Parco d'Orleans II - 90128 Palermo, Italy*

Abstract

The subject of this present work is a group of nine historical pictures shot in Palermo by the Sicilian photographer E. Interguglielmi in 1912. They are nine *matte*-collodion prints mounted on the original cardboard supports and all of them show *foxing* stains affecting the paper surface.

In order to characterize the chemical composition of the supports and investigate *foxing* spots, non-destructive and micro-destructive analysis were carried out. X-Rays Fluorescence (XRF) analysis was used to characterize the elemental composition of all the mounting boards, allowing a comparison between the foxing spots and non-affected areas. Laser Induced Breakdown Spectroscopy (LIBS) was used to investigate the presence of lower atomic number elements, not detectable by XRF, while SEM imaging allowed the investigation of surface appearance and nature of original paper samples from the cardboards.

Keywords: Foxing; Fungi; XRF; LIBS; SEM

* Corresponding authors: Maurizio Bruno: E-mail: maurizio.bruno@unipa.it

3. Experimental

3.1. *Fibres identification*

Herzberg is an iodine-based stain useful to differentiate between rag, groundwood, and chemical wood pulps and is prepared mixing two solutions: Solution A (50 g of dry ZnCl_2 in 25 mL of water) and Solution B (0.25 g of iodine and 5.25 g of KI in 12.5 mL of water). Applying a few drops of the stain to the prepared fibre suspension on a microscope slide, the different colour of the samples allow the identification of the fibres: all chemical wood pulps, whether bleached or unbleached, acquire a blue tint, rag pulp stains pink, groundwood and in general lignin rich pulp, is a vivid yellow. The paper suspension was obtained tearing paper fragments into small pieces, covering them with deionized water and bringing to the boil on a hot plate. Then, water was added and the sample shaken vigorously until the paper has been thoroughly disintegrated. After applying a few drops of the stain to the fibre field on the slide, the colour developed allows the identification of the fibres (ASTM D1030-95. 2007).

3.2. *Acidity measurements*

Measurements were taken on a fibre suspension obtained soaking small detached paper fragments in deionized water for 24h and using a flat tipped glass body pH electrode.

3.3. *XRF measurements*

A portable XRF system, namely the ArtTAX 400 spectrometer from Bruker AXS, was used to acquire XRF spectra. It was equipped with a Mo ($K\alpha = 17.5$ keV) low-power excitation tube (with a 100 μm thick beryllium window), enclosed by a safety radiation shield. A filter disk system, put before the X-ray beam placed between the X-ray tube and the sample, can be used in order to attenuate the Bremsstrahlung radiation and to reduce the diffracted component of the X-ray beam. A pinhole system in the X-ray source provided a collimated beam on the sample making the instrument suitable to perform spatially resolved multi-elemental analysis on three-dimensional structures.

The detector was an XFlash 1001 (a Peltier cooled silicon drift detector) with high speed, low noise electronics, and a FWHM energy resolution < 145 eV at the Mn $K\alpha$ energy (5.9 keV) with an active area of 5 mm^2 and an 8 μm beryllium window. The detection head contains the detector and the X-ray tube, fixed on a movable tripod allowing independent vertical and horizontal movement, and its power supply. The mobile XRF moving head includes also a micro-camera for the positioning of the incident beam on the sample.

Helium flux system, reducing the photoelectric absorption of the sample characteristic X-rays by

the air molecules, allows an improvement in the detection of light elements.

The geometry between primary beam, sample, and detector is fixed at 0°/40° relative to the perpendicular of the sample surface (Fontana et al. 2014). Measurement setup was as follows: tube voltage 40 kV; current 700 μ A; acquisition time 100 sec (real time acquisition); no filter disk between the X-ray tube and the sample; He flow rate 1.6 L min⁻¹, lateral resolution 0.65 mm, with a distance between sample and detector around 1 cm. The setup parameters were selected to have a good spectral signal and to optimize the signal to noise ratio (SNR).

In order to overcome XRF limitations in detecting and measuring lighter elements such as Mg and Na, LIBS measurements were performed on a fragment detached from one of the photos. Only this sample has been selected for this kind of analysis since LIBS operates in a micro-destructive way.

3.4. LIBS measurements

The portable equipment for the LIBS measurements is the MOBILE Dual-pulse Instruments (MODi, from Marwan Technology). It integrates a double pulsed Q-Switched Nd:YAG laser (Lotis, mod. LS-2131D) emitting two collinear laser pulses at 1064 nm, whose energy can be set by varying the lamp flash voltage. The pulsed energy focused on the sample surface is within 50- 120 mJ with a maximum repetition rate of 10 Hz and a reciprocal delay adjustable from 0 to 60 μ s. High lateral spatial resolution of the LIBS measurements corresponds to the dimensions of the micro-crater left by the laser on the sample surface. The micro-crater diameter, whose dimensions are related to the laser energy, does not exceed 100 μ m. The small size of the crater also allows for a high lateral spatial resolution of the LIBS analysis (Angeli et al. 2006; Anglos et al. 1997).

LIBS equipment allows to carry out measurements on samples located inside an experimental chamber (as in our case) or outside through an external arm. The experimental chamber is equipped with a XYZ motorized table and an optical microscope for exact positioning of the sample at the focus of the laser beams. LIBS signal is collected and transferred through a Y bundle SiO₂ optical-fibre to a compact Echelle spectrometer (Andor, ME5000) coupled to an Intensified Charge Coupled Device (ICCD, Andor, mod. iStar) for the spectral acquisition.

An integrated personal computer manages the sample visualization and positioning, the experimental settings of the laser and spectral acquisition parameters – number of averaged spectra, Gate Pulse Delay (GPD), Gate Pulse width (GPW) and Multi Channel Plate Gain (MCPG).

With the aim to optimize the LIBS signal, the laser pulse energy has been varied in order to identify and select the most appropriate ones to perform a simultaneous measurement of the chemical elements (Alberghina et al. 2015). In particular, energy has been chosen evaluating results from measurements performed at 11.5, 12.5, 13.0, and 14.0 J. Since it was not possible, even at the

lowest energy laser pulse used, to obtain a depth profile due to the small thickness of the sample, the value of 14.0 J (with GPD 0.4, GPW 2 μ s, single shot) has been chosen for measurements. These energy values allowed reaching the best signal to noise ratio, allowing detection of all light elements of interest (Na, Mg, Ca).

Table 3 shows the considered atomic emission lines, chosen among those not affected by self-absorption (Handbook of basic Atomic Spectroscopic data, NIST – <http://www.physics.nist.gov>) for calcium, magnesium and sodium. The peak intensity variation of the main spectral lines has been evaluated along the different typology of the surface within the sample, both not degraded and degraded by *foxing* stain.

3.5. Microbiological analysis

Microbiological tests were carried out in order to verify the presence, over the cardboards' surface, of living microorganisms.

Sampling was done by gently rubbing on the cardboard N. 1 surface in foxed and unaffected areas with disposable sterile cotton swabs; this was followed by inoculation in sterile petri dishes on *Sabouraud* dextrose/maltose agar (SD/SM), specific medium for the fungal growth, and *Nutrient Agar* (NA) medium for fungi and bacteria growth. Petri dishes were put in a thermostatic incubator at constant conditions (26°C, 80-90% RH). No growth of microorganism occurred.

3.6. SEM

To obtain SEM imaging, micro-samples from the surface layer of the cardboards affected by *foxing* were gently attached on stubs with carbon adhesive and analysed using a Phenom Pro Desktop SEM (Magnification range: 80 - 100,000x, Acceleration voltages: 5 kV and 10 kV - Detector backscattered-electron BSED). SEM setups allowed the mapping of paper surface without prior preparation by means of metallization.

Fig. S1. Comparison between LIBS spectra acquired, with the same temporal parameters, on not degraded paper (dark gray line) and on *foxing* stain (red line): *a)* zoom of Ca emission lines in 392 ÷ 398 nm spectral range; *b)* zoom of Mg emission lines in 278 ÷ 281 nm spectral range; *c)* zoom of Na emission lines in 584 ÷ 596 nm spectral range.

Fig. S2. Principal Components Analysis (PCA) and projection of the initial variables on PC plane. Empty and full symbols indicate paper and *foxing* area measurements, respectively.

Fig. S3a. SEM image of cardboard sample N.I. 9. Unaffected area.

Fig. S3b. SEM image of cardboard sample N.I. 9.
Unaffected area.

References

- Alberghina MF, Barraco R, Brai M, Fontana D, Tranchina L. 2015. LIBS and XRF analysis for a stratigraphic study of pictorial multilayer surfaces. *Period Mineral.* 84:569-589.
- Angeli L, Arias C, Cristoforetti G, Fabbri C, Legnaioli S, Palleschi V, Radi G, Salvetti A, Tognoni E. 2006. Spectroscopic techniques applied to the study of Italian painted neolithic potteries. *Laser Chem.* Article ID 61607, 7 pages, DOI:10.1155/2006/61607.
- Anglos D, Couris S, Fotakis C. 1997. Laser diagnostics of painted artworks: laser-induced breakdown spectroscopy in pigment identification. *Appl Spectrosc.* 51:1025-1030.
- ASTM D1030-95. 2007. Standard test method for fiber analysis of paper and paperboard (Withdrawn 2011). ASTM International, West Conshohocken, PA.
- Fontana D, Alberghina MF, Barraco R, Basile S, Tranchina L, Brai M, Gueli A, Troja SO. 2014. Historical pigments characterization by quantitative X-ray fluorescence. *J Cult Herit.* 15:266-274.