

DOCTORAL THESIS

Nondestructive multi-element analysis of colorants for forensic applications and artwork authentication

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**Nondestructive Multi-element Analysis of Colorants for
Forensic Applications and Artwork Authentication**

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**A thesis submitted in partial fulfillment of the requirements
for the Degree of
Doctor of Philosophy**

**Principal Supervisor: Prof. CHEUNG Nai Ho
Hong Kong Baptist University**

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Abstract

Chemical analysis of colorants for authentication purpose is in great demand. One application is the authentication of works of art because the value and volume of artwork sales is huge and growing. Another application is the forensic examination of laser-printed documents because of the availability of high quality laser printers on the one hand and the proliferation of laser-printed documents on the other. In both applications, non-destructive elemental analysis is required to complement the organic analysis and the subjective morphological analysis. Portable x-ray fluorescence (XRF) was shown to be an applicable technique but its sensitivity was not adequate to tell some ink brands apart especially when the printed letters were smaller than font size 20. In the case of overprints, the depth resolution of XRF was not adequate to tell the printing sequence either. We showed that the new technique of laser-excited atomic fluorescence (LEAF) of laser ablation plumes (PLEAF) nicely complemented the limited sensitivity and spatial resolution of XRF. For example, in the PLEAF analysis of laser-printed ink, the relative limit of detection (LOD) was down to tens of ng/g and the mass LOD was down to atto-mole. Etch rate was down to hundreds of nm per shot over a spot of about 100 μm in diameter. This kind of crater was not observable under the optical microscope. In PLEAF analysis, the photoacoustic signal was measured in real-time in order to monitor the minute amount of mass ablated. Our results showed that the sensitivity of this kind of indirect weighing was down to pg. We applied PLEAF to analyze four brands of laser-printed inks and we used photoacoustic monitoring to gauge sample destruction. We successfully sorted the four inks, determined the printing sequence of overprints, and characterized aged prints, all with non-observable damage to the sample. We also applied the technique to sort two brands of Chinese red seal cinnabar inks that looked identical in color. While “we” was used to indicate group work, investigations done by others were clearly clarified in this thesis.

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