Non-destructive recovery of historical ink chemistry using machine learning

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Iron gall inks, widely used in Europe for centuries, are complex multi-component mixtures whose elemental composition reflects the raw materials, manufacturing practices, and historical context of their production. In favorable cases, detailed chemical characterization of ink traces can support hypotheses concerning provenance and authorship. Here, we present an interdisciplinary analytical workflow that combines conservation-compatible sampling, high-sensitivity elemental analysis, and machine-learning-assisted data interpretation to reconstruct the elemental fingerprints of historical inks directly from manuscripts. Chemical information is transferred non-destructively from the inked surface to indicator papers soaked with bathophenanthroline, in accordance with established conservation protocols. The indicator papers are then analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which provides multi-elemental information with sub-μg/g detection limits. Classical and modern machine learning methods are used to model the relationship between ink composition and the chemically transferred signal preserved in the indicator, serving as a proof of concept for the task of non-destructive recovery of historical ink chemistry. The methodology is presented on historically significant manuscripts, including Nicolaus Copernicus' handwritten notes. Additional information obtained from a group of heavily corroded ink samples supports identification of harmful components of the writing agents and assessing safety of the precious historical objects.

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