

Step by step: Modelling as a first key to introduce an indirect method of studying heritage inks

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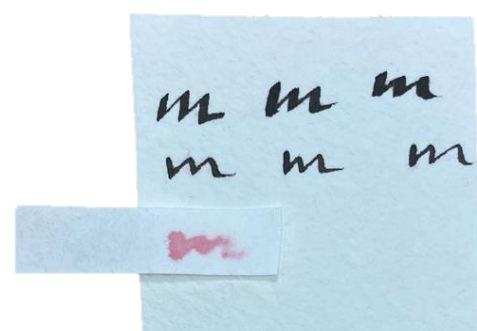
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Iron gall inks had been used since ancient times. The most important historical manuscripts, maps, documents and the most famous drawings of our history were created using these inks obtained by mixing metal compounds with extracts of tannin-rich plants and Gum Arabic. This dark solutions contained complexes of 3,4,5-trihydroxybenzoic acid (gallic acid) with metal ions added in the form of salts (vitriols). Green vitriol was the most common, but not the only available source of the metal ions used. Although the basis of all inks was constant: a mixture of solutions containing metal ions with extracts of gall nuts, the details of recipes varied, significantly influencing the final composition. It is frequently observed that even in a single manuscript inks of variable elemental composition can be distinguished by chemical analyses.

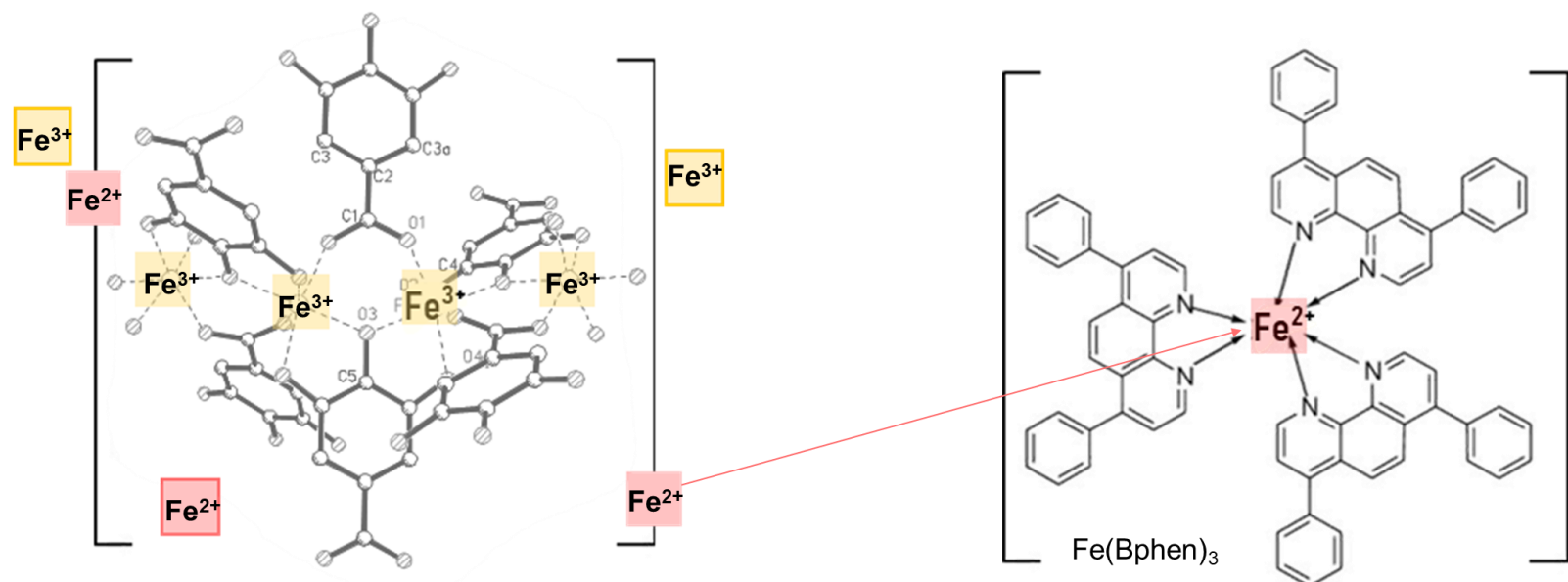
Iron Gall Ink Test Papers/PELs

Indirect method of studying the composition of iron-gall inks??

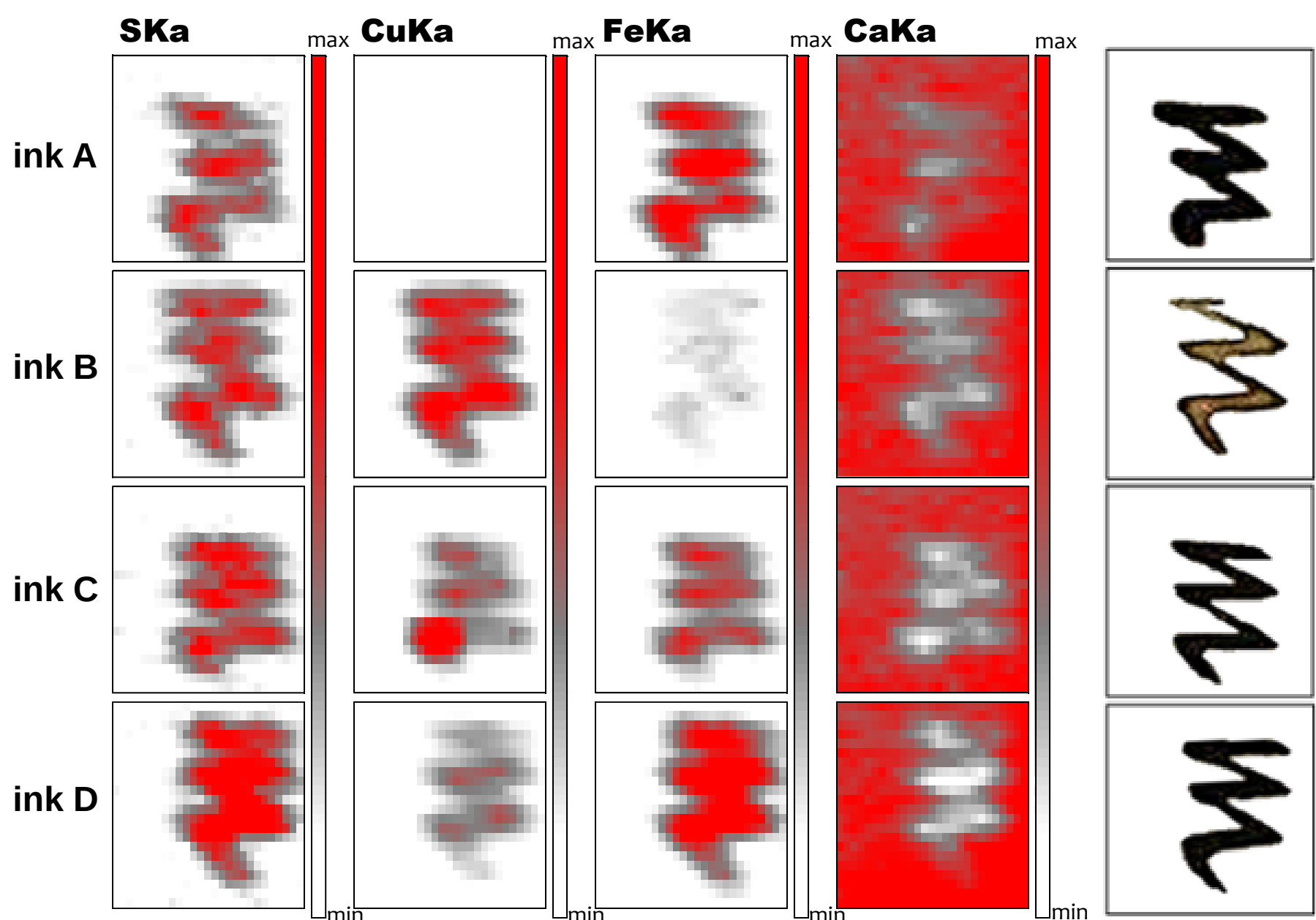
- Feasibility of a multi-instrumental approach in the study of historical manuscripts is demonstrated in numerous publications. However, direct access to the object is always required to perform measurements.
- A novel approach which differs from the earlier concepts is proposed. It aims to examine used indicator papers introduced by Neevel for screening manuscripts written with iron gall inks.
- Following the results of the preliminary research, it seems possible to involve the use of Iron Gall Ink Test Papers (indicator papers) for indirect studies of iron gall ink inscriptions.
- Processes which occur during the contact of the tested areas with indicator papers allow partial immobilization of elements migrating from inks and their detection using sensitive analytical techniques.



Colorimetric effect in the indicator paper in the presence of iron (II) ions in ink - formation of the colorful Fe-Bphen complex (contact time = 30 s)



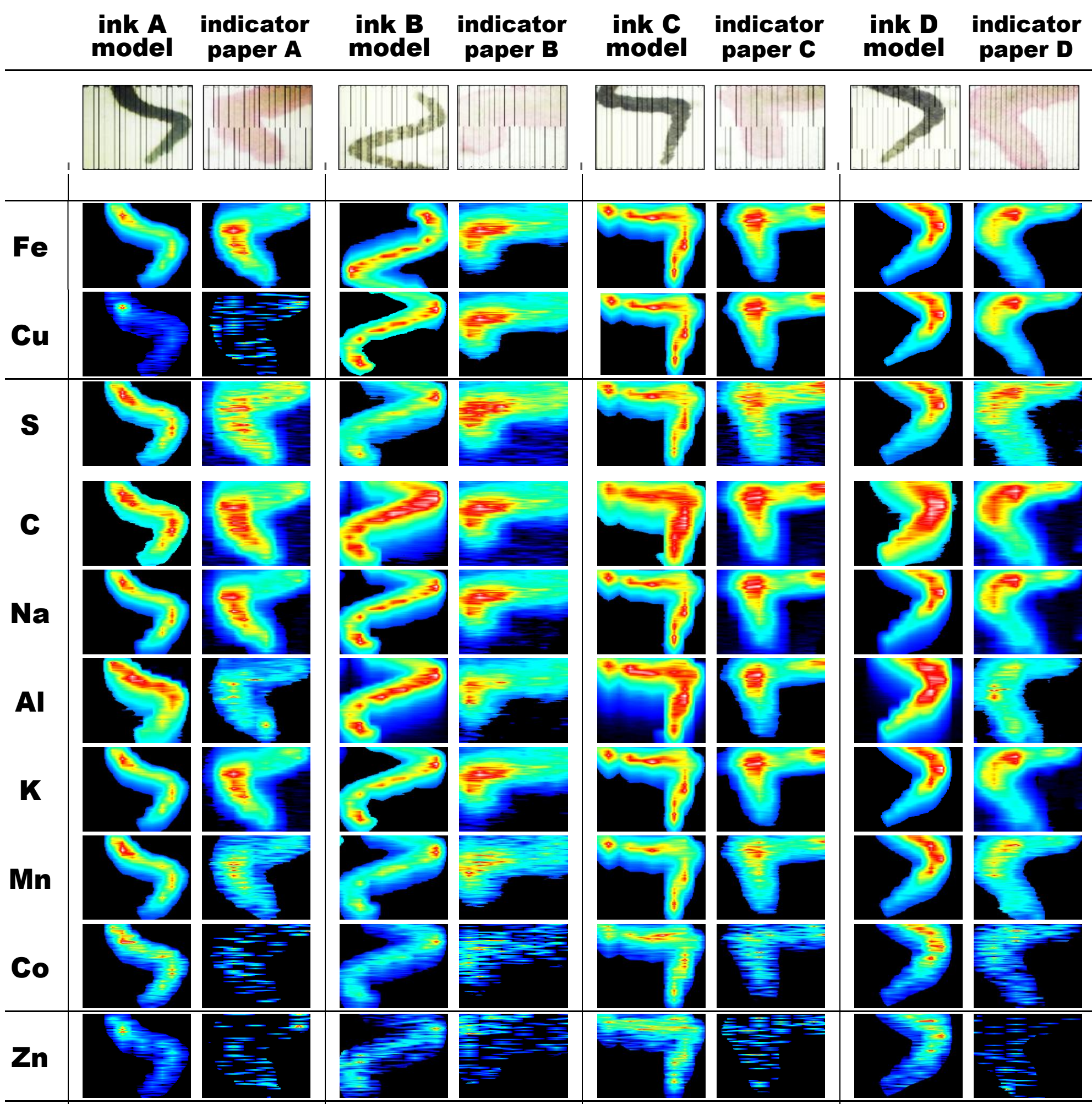
Exemplary XRF measurements of 4 model inks containing Fe and Cu



- X-Ray Fluorescence (XRF) mapping of the inscription on paper
- Fe, Cu and S detected in the inscription
- Ca detected in the paper

XRF parameters:	ELIO Bruker spectrometer
Operating voltage	50 kV
Current	80 µA
Map size	10 mm x 10mm
Spot size	1 mm ²
Time per spot	2 sec

Exemplary LA-ICP-MS measurements of 4 model inks containing Fe and Cu and indicators



- Main elements of the inks (Fe, Cu, S) detected, analogical to XRF
- Distribution of other elements, originating from the composition and impurities of the substrates, also observed
- All elements present in the inks also detected in the indicators

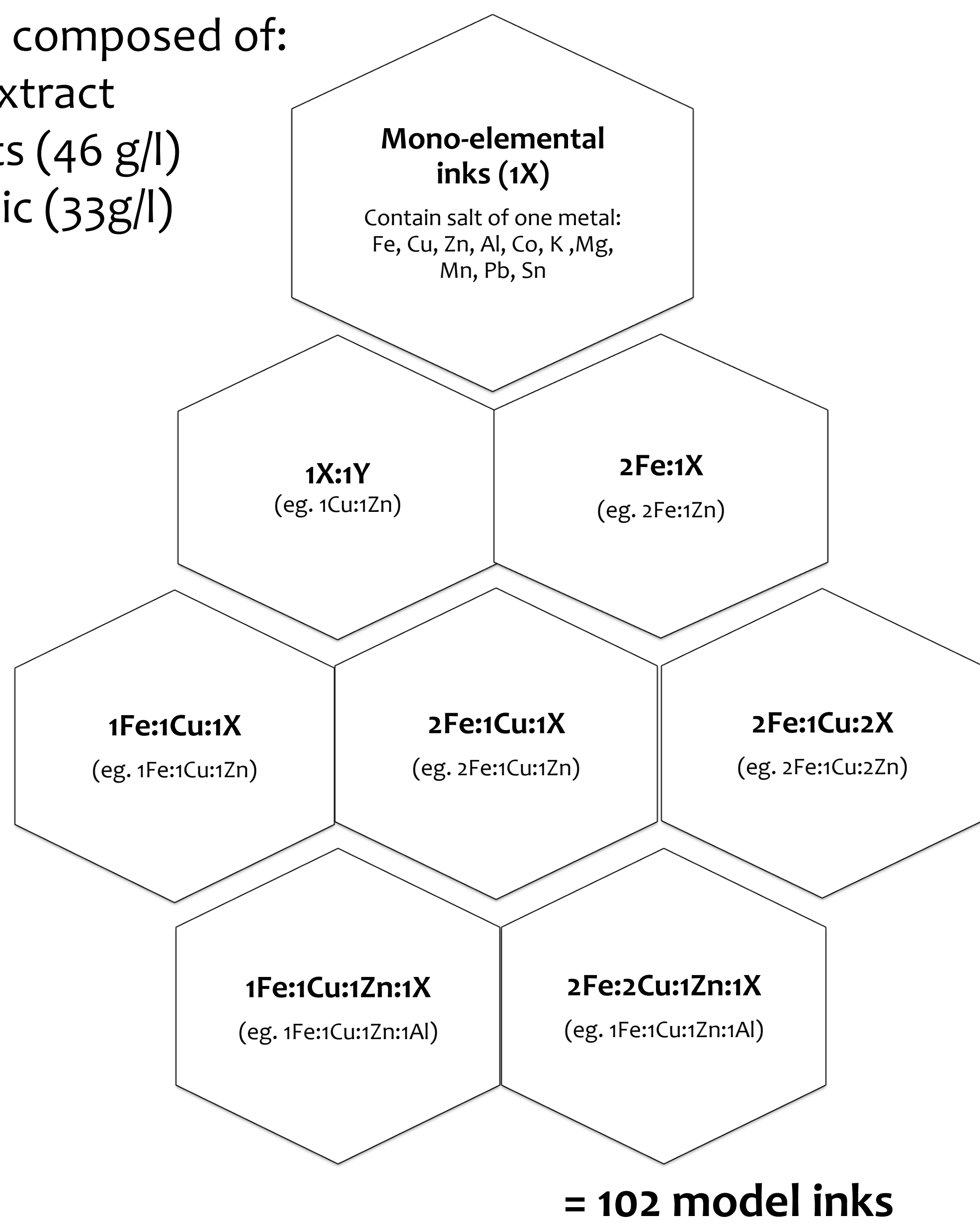
LA- ICP – MS parameters:	LSX-213 laser ablation system, CETAC NexION 300D spectrometer, Perkin Elmer
Plasma power	1400 W
Carrier gas flow (Ar)	0.9 l/min
Sweeps	1
Readings	7797
Repetitions	1
Dwell time	5 ms

Model inks

Preliminary results demonstrating migration of various elements to the indicator papers motivated creation of a base of inks with varying and well described compositions, allowing for a systematic study.

All inks were composed of:

- Gall nut extract
- Metal salts (46 g/l)
- Gum arabic (33g/l)



Model inks and gall-nuts (phot. B. Wagner)

Project ALINA: Spectral Analysis of Legacy Inks using machine learning

- Preliminary results suggest high complexity of the processes occurring during the transfer of chemical information from inks to indicator papers
- The aim of the ALINA project is to engage machine learning methods in encoding the intricate signals
- The actual composition of the obtained inks and migration of their compounds into the indicator papers will be studied with the use of the spectral methods, including LA-ICP-MS
- Results of the measurements will form a database used by the machine learning algorithms

Literature:

- J.G Neevel, B.Reissland, Bathophenanthroline indicator paper, Papier Restaurierung (2005) 6: 28–36;
- J.G.Neevel, Application Issues of the Bathophenanthroline Test for Iron(II) Ions, Restaurator (2009) 30:3-15;
- B.Wagner, E.Bulska, On the use of laser ablation inductively coupled plasma mass spectrometry for the investigation of written heritage, J. Anal. At. Spectrom. (2004) 19:1325-1329;
- B.Wagner, A.Czajka, Non-invasive approximation of elemental composition of historic inks by LA-ICP-MS measurements of bathophenanthroline indicators, Talanta (2021) 222:121520

