The secret of black marker pens:
Identification workflow with non-invasive hyperspectral and macro X-ray fluorescence imaging techniques

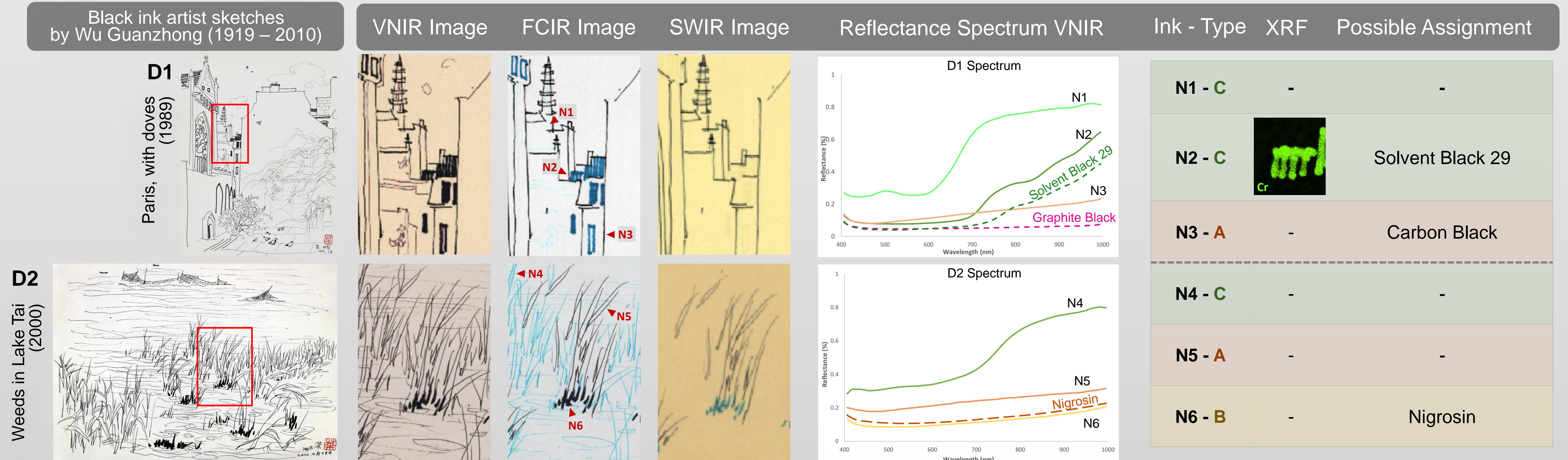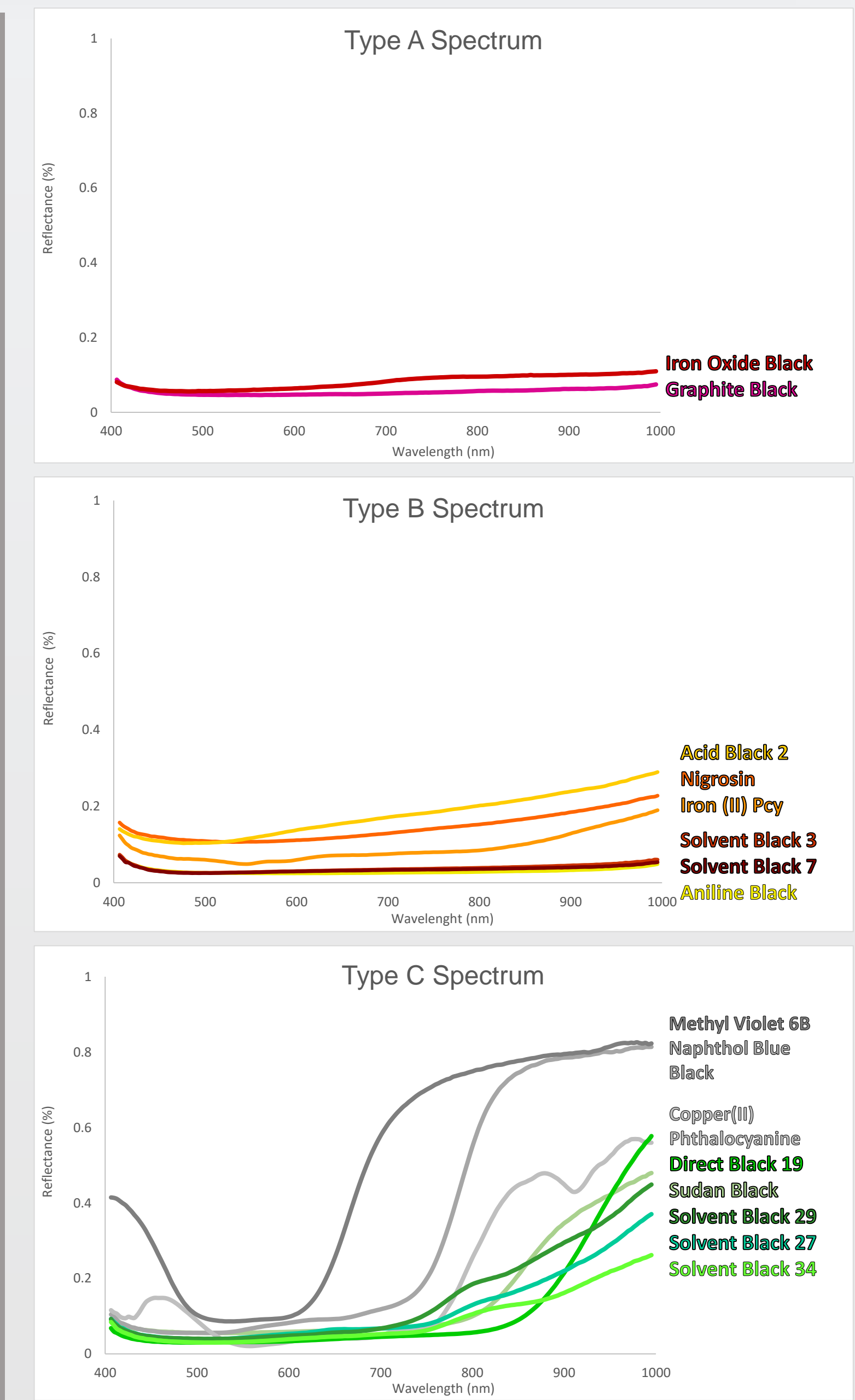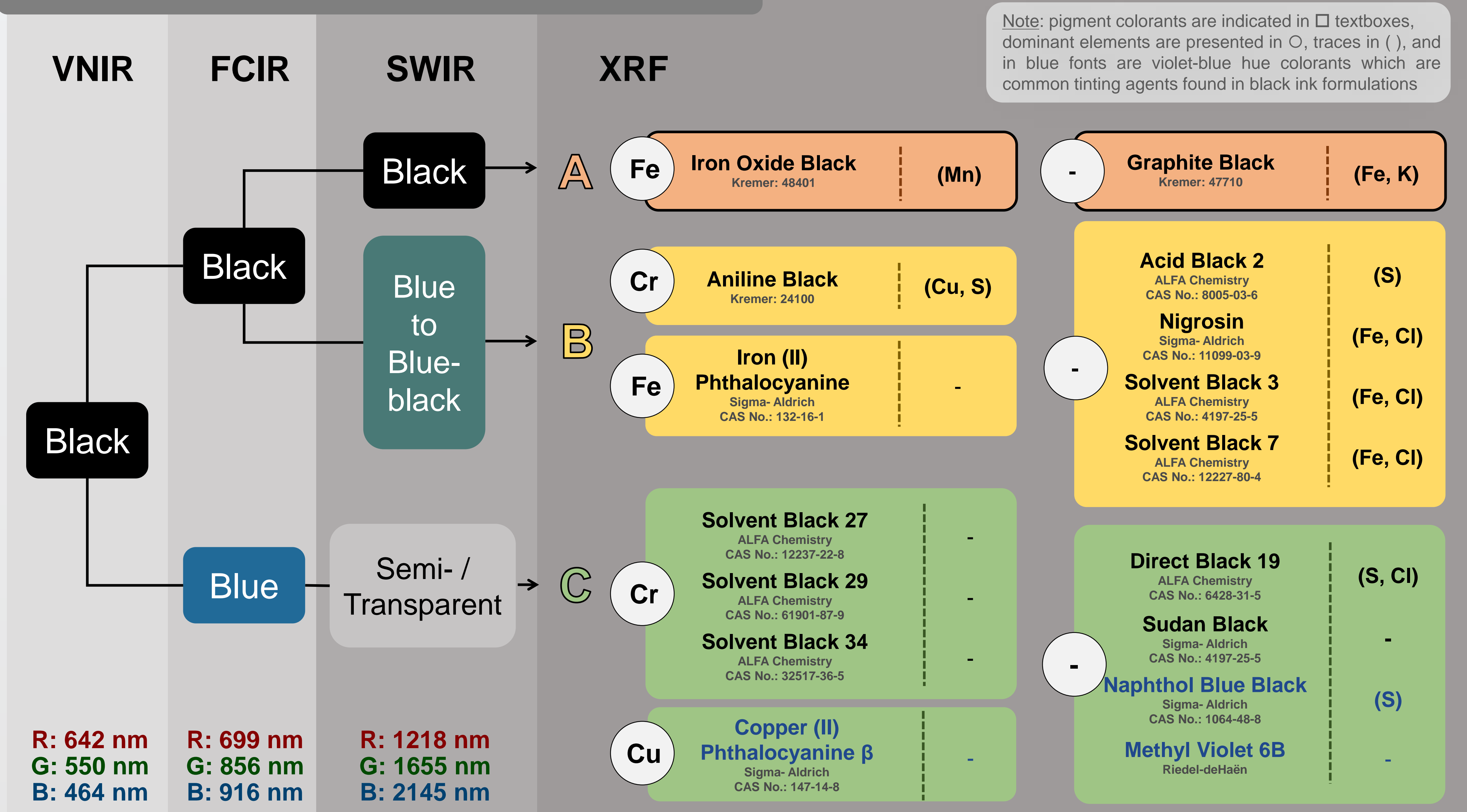Ethel Yi-man LOWE§, Rita Wai-tung LIU§, Gordon King-wai CHIU† and May Chui-in LONG§

Background and Objectives

- Marker pens were popularized in the 1950s, a common and convenient writing stationery, widely used in artist drawings, illustrations, architectural plans and archival documents
- Blue and black inks are well-studied in the field of forensic science but the analytical methods usually involve sampling which is not always applicable to cultural heritage objects
- Media identification is fundamental in the development of preservation plans
- This study aims to establish a workflow by a combination of the non-invasive techniques - **hyperspectral imaging (HSI)** and **macro X-ray fluorescence (MA-XRF)** analysis to characterize and attempt to identify some of the commonly found **black colorants in marker pens and modern drawing inks**

Method

- **13 commonly occurring black colorants** in modern black inks were studied
- Dry pigments were mixed with gum arabic, dyes were dissolved in ethanol or water, then applied on off-white 130 gsm drawing paper
- HSI data was collected with HySpex VNIR-1800 for the visible to near infrared range 400-1000 nm and HySpex SWIR-384 short-wave infrared from 930-2500 nm
- **False Colour (FC) images** were created with the VNIR images by adjusting the wavelength display channels (nm) : R → 699, G → 856 and B → 916
- XRF scan of the colorants was performed with the M6 Bruker Jetstream (Rh anode, 50 kV, 600 µA, air-path)
- A **flowchart** was developed based on the FCIR, SWIR images and elemental results of the colorants which could be **summarized into 3 categories**

Flowchart for the categorization of black colorants

Note: pigment colorants are indicated in □ textboxes, dominant elements are presented in ○, traces in ( ), and in blue fonts are violet-blue hue colorants which are common tinting agents found in black ink formulations

VNIR FCIR SWIR XRF

A — Fe — Iron Oxide Black (Kremer: 48401) — (Mn) | - — Graphite Black (Kremer: 47710) — (Fe, K)

B
- Cr — Aniline Black (Kremer: 24100) — (Cu, S)
- Fe — Iron (II) Phthalocyanine (Sigma-Aldrich, CAS No.: 132-16-1) — -
- Acid Black 2 (ALFA Chemistry, CAS No.: 8005-03-6) — (S)
- Nigrosin (Sigma-Aldrich, CAS No.: 11099-03-9) — (Fe, Cl)
- Solvent Black 3 (ALFA Chemistry, CAS No.: 4197-25-5) — (Fe, Cl)
- Solvent Black 7 (ALFA Chemistry, CAS No.: 12227-80-4) — (Fe, Cl)

C
- Cr — Solvent Black 27 (ALFA Chemistry, CAS No.: 12237-22-8) — -
- Solvent Black 29 (ALFA Chemistry, CAS No.: 61901-87-9) — -
- Solvent Black 34 (ALFA Chemistry, CAS No.: 32517-36-5) — -
- Cu — Copper (II) Phthalocyanine β (Sigma-Aldrich, CAS No.: 147-14-8)
- Direct Black 19 (ALFA Chemistry, CAS No.: 6428-31-5) — (S, Cl)
- Sudan Black (Sigma-Aldrich, CAS No.: 4197-25-5) — -
- Naphthol Blue Black (Sigma-Aldrich, CAS No.: 1064-48-8) — (S)
- Methyl Violet 6B (Riedel-deHaën) — -

VNIR — R: 642 nm, G: 550 nm, B: 464 nm
FCIR — R: 699 nm, G: 856 nm, B: 916 nm
SWIR — R: 1218 nm, G: 1655 nm, B: 2145 nm

Type A Spectrum — Iron Oxide Black, Graphite Black

Type B Spectrum — Acid Black 2, Nigrosin, Iron (II) Pcy, Solvent Black 3, Solvent Black 7, Aniline Black

Type C Spectrum — Methyl Violet 6B, Naphthol Blue Black, Copper(II) Phthalocyanine, Direct Black 19, Sudan Black, Solvent Black 29, Solvent Black 27, Solvent Black 34

Black ink artist sketches by Wu Guanzhong (1919 – 2010)

D1 — Paris, with doves (1989)
D2 — Weeds in Lake Tai (2000)

D1 Spectrum — N1, N2, Solvent Black 29, N3, Graphite Black

D2 Spectrum — N4, N5, Nigrosin, N6

Ink - Type	XRF	Possible Assignment
N1 - C	-	-
N2 - C	Cr	Solvent Black 29
N3 - A	-	Carbon Black
N4 - C	-	-
N5 - A	-	-
N6 - B	-	Nigrosin

Application and Results

- 2 black ink artist sketches (D1-2) from the **Wu Guanzhong collection of the Hong Kong Museum of Art** were scanned with HSI and XRF
- **3 distinctive inks are observed in each of the drawings**, evidently in their FC images: inks N1-3 in D1 and inks N4-6 in D2
- Results would suggest **Category A – pigment based inks**, **Categories B and C – dye based inks**
- Following the flowchart, reflectance spectrum of each ink is compared with reference materials, and possible assignments are determined for **N2 – Solvent Black 29 (dye)**, **N3 – carbon (graphite) black** and **N6 – Nigrosin (dye)**
- N3 is in fact a dark blue ink, this is replicated by a peak at around 500 nm and shoulder above 600 nm in its reflectance spectrum

Discussion and Future Work

- Imaging result provides **insight to the artistic creative process** of the artwork
- Analysis of a **combination of FCIR and SWIR images** has proved to be effective to **differentiate between the various black inks** present in an artwork
- The flowchart categorization of inks may help to evaluate the vulnerability of an artwork, **to distinguish between black pigment and dye based inks**, as the latter are more moisture sensitive and prone to fading and/or discoloration
- Some **black dye colorants exhibit distinctive spectral features and/or elemental component** which show potential for media identification
- Building a media reference library on colorants in their chemical forms, as well as commercial drawing inks and pens will aid material studies of the contemporary museum and archival collection
- **Ink deterioration and fading, mixtures and concentrations** are all factors which complicate ink identification, **further study** is required to investigate and verify their impacts on the categorization and identification flowchart

Selected References

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