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# Visualising iron gall ink underdrawings in sixteenth century paintings in-situ by micro-XRF scanning (MA-XRF) and LED-excited IRR (LEDE-IRR)

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## Abstract

Until today, iron gall ink is classified as an exceptional underdrawing material for paintings. Its study and definite identification is usually based on invasive analysis. This article presents a new non-destructive approach using micro-X-ray fluorescence scanning (MA-XRF), LED-excited IRR (LEDE-IRR) based on a narrow wavelength-range of infrared radiation (IR) for illumination and stereomicroscopy for studying and visualising iron gall ink underdrawings. To assess possibilities and limits of these analytical techniques, the approach was tested on panel paintings by Hans Holbein the Elder and Giovanni Battista Cima da Conegliano. Results are compared to invasive examinations on cross-sections using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The holistic setup could successfully visualise iron gall ink underdrawings, allowing to harness the formerly invisible underdrawing lines for interdisciplinary studies.

**Keywords:** Iron gall ink, Underdrawing, Panel paintings, MA-XRF, IRR, LEDE-IRR, Microscopy, Holbein the Elder, Cima da Conegliano, Sixteenth century

## Introduction

Iron gall ink has been used as a drawing and writing material from roughly around third century BC and was widely spread since Medieval times [1, 2].<sup>1</sup> The ink is a complex reaction product of ferrous sulphate from vitriol and soluble gallotannins from galls, which was utilised in an aqueous solution with a gum binding agent [2]. Despite being the most important ink in European history until the nineteenth century, it has rarely been identified as an underdrawing material for paintings. However, the diversity of origin and dating of the few paintings with verified iron gall ink underdrawings could hint at a more widespread use than currently assumed.

Since underdrawings of paintings are usually covered by several heterogenous painting layers, they are commonly studied by infrared radiation-based (IR) methods such as infrared reflectography (IRR). Because IRR is particularly sensitive for carbon-based underdrawing materials, iron gall ink underdrawings only rarely become visible by IR-based techniques [1] (p. 31). Until now, reliable identification of iron gall ink underdrawings has always been based on invasive analysis, e.g. [3] (p. 75), [4] (p. 134) or [5] (p. 20), which is not always applicable due to various reasons.

This study is part of a research project on the non-destructive analysis of non-carbon-based underdrawings at the Städel Museum Frankfurt in cooperation with the

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<sup>1</sup> First evidence on the use of iron gall ink could be found by particle-induced X-ray emission (PIXE) analysis on Egyptian papyri originating from the 3<sup>rd</sup> to first century BC, whereas the first recipe from the European area is dated into the seventh century AD [2].

Stuttgart State Academy of Art and Design and the Städel Cooperation Professorship at the Institute of the Art History at the Goethe-University Frankfurt. The analysis approach combines micro-X-ray fluorescence scanning (MA-XRF) with a novel advanced use of IRR, that uses IR-LEDs with a narrow wavelength range for illumination (LEDE-IRR). Results are compared to invasive scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX) on cross-sections. This paper aims to present and evaluate possibilities and limits of MA-XRF and LEDE-IRR as a routine approach for studying iron gall ink underdrawings, either pure or in mixture with carbon black pigments, focussing on the impact of measurement parameters, value of identifying trace elements and in-depth post-processing routines.

The main inorganic component of iron gall ink is vitriol, an iron sulphate ( $\text{FeSO}_4$ ) with varying impurities of various metal sulphates based on Cu, Mn, Zn, Al, K or Mg. The proportion of these components varies depending on the mining site and extraction method of the vitriol used [2, 6, 7]. For instance, while *vitriolum goslar-ensis*, originating from Goslar (Germany), has a very high amount of  $\text{ZnSO}_4$  (11%), *vitriolum romanum* does not contain Zn [6] (p. 130).<sup>2</sup> XRF based analytical techniques such as MA-XRF are highly sensitive for the identification of mid-range chemical elements such as Fe, Cu, Mn and Zn [8] (p. 763). MA-XRF scanning has proven to be a rewarding non-invasive and in-situ analysis technique for historical paintings, e.g. [8–13], after the introduction of mobile X-ray tube-based MA-XRF instruments [10, 11]. Main principles of XRF can be found elsewhere [14]. In general, the distribution of mid-range elements can be visualised by acquiring several thousands to millions single XRF spectra in a two-dimensional scan. From this, chemical information on surface and sub-surface layers can be derived, allowing to infer on pigments and the technological build-up of paintings. Although suitable, MA-XRF has not been consciously used to analyse and visualise iron gall ink underdrawings in paintings until today. First attempts to study non-carbon-based underdrawings that are invisible in conventional IRR were performed with Point- $\mu$ -XRF (P- $\mu$ -XRF), e.g. [15]. The main disadvantage of P-XRF is, that elemental signals cannot be unambiguously assigned to specific sub-surface layers in the heterogenous multi-layered structure of paintings. Further, Fe is not only the main inorganic component of iron gall inks but also of ochre pigments, which were not only also used for underdrawing paintings but also often appear as pigments in paint layers. Therefore, trace elements present in iron gall ink such as Cu and Zn become

highly important to distinguish between both materials. P-XRF analysis on inorganic components of iron gall ink on parchment and paper, has been studied by Krekel [2] and Hahn [16], the latter resulting in a fingerprint model based on XRF data quantification [17, 18], that uses ratios of impurity metals in vitriol such as Cu, Mn and Zn related to Fe as main component to distinguish between different inks [17, 18]. Unfortunately, this fingerprint model is hardly applicable on underdrawings, as these are usually completely covered by paint layers. Nevertheless, the joint presence of elements such as Cu and Zn could distinguish between different Fe-containing underdrawing materials such as ochres and iron gall inks. In various studies, lost scriptures written with iron gall ink in palimpsests [19, 20] or iron gall ink underdrawings underneath manuscript illuminations [21] could be successfully visualised by means of MA-XRF. Furthermore, the underdrawing of Leonardo da Vinci's "Madonna of the Rocks" from the National Gallery London could be unravelled by the distribution of a Zn-containing material, that has not yet been further specified [22].

Material identification of an underdrawing material could be achieved by combining different analytical techniques which are able to gain information on different characteristics. Using IRR with different narrow wavelength ranges (LEDE-IRR) (Additional file 1: Suppl. 1), different IR reflectance properties of historical underdrawing materials can be studied. According to recent reflectance measurements, iron gall inks absorb IR radiation up to 1200 nm [23] (p. 58) (Additional file 1: Suppl. 2),<sup>3</sup> while ochre already become transparent at 850 nm [25] (p. 16). An iron gall ink underdrawing could be thus determined, if the underdrawing lines absorb radiation up to 1200 nm and become invisible in higher wavelengths. A similar approach was first tested in the 1990s with filter sets, that transmit only certain wavelengths, but was not pursued because resulting images were very dark [26, 27]. A novel and more promising concept was recently developed by Geffken, Krekel and Dittmar at the Institute for Conservation Sciences of the State Academy of Art and Design Stuttgart in cooperation with the Steinbeis Transfer Centre of Aalen University [23]. IR-LED lights with narrow wavelength ranges at 880 nm, 940 nm, 1060 nm, 1300 nm and 1550 nm for illumination (LEDE-IRR), that can either be used individually or in combination (Additional file 1: Suppl. 1), proved to enable a better detection of underdrawing materials such as iron gall ink [23] (p. 124). The spectral sensitivity of the Osiris, which is equipped with an InGaAs sensor, is stated

<sup>2</sup> Hickel locates the mining site of *vitriolum romanum* on the Isle of Elba, although it could likely be a trade name for a product with varying origins.

<sup>3</sup> The iron gall ink used for the measurements on the IR reflectance properties was produced according to recipe 208 and recipe 211 of the Liber illuministarum, which was written around 1500 in the Benedictine Monastery at Tegernsee, Southern Germany [24].

**Table 1** Overview and general information of the examined panel paintings

Artist	Title	Date	Inv. No.
Hans Holbein the Elder	Tree of Jesse <sup>a</sup>	1501	HM 6
Hans Holbein the Elder	Bearing of the Cross <sup>a</sup>	1501	HM 15
G. B. Cima da Conegliano	Virgin and Child	ca. 1500–1504	852

<sup>a</sup> Part of the Frankfurt Dominican Altarpiece

to range between 900 and 1700 nm [28]. Novel transmission measurements by Geffken and Dittmar could prove, that the Osiris camera is already sensitive for lower wavelength area even though to a considerably lesser extent [23] (p. 33). Therefore, IR-LED lights were built in accordance to the IR sensitivity of the Osiris camera. Especially by adjusting the irradiance intensities of the IR-LED lights, wavelengths beyond the InGaAs sensor's given sensitivity, such as 880 nm, could be sufficiently detected by the Osiris camera [23] (p. 87–91).

## Materials and methods

### Panel paintings

Three panel paintings from the collection of the Städel Museum were chosen for the study, as they only partly showed underdrawing lines during preliminary conventional IRR with halogen lights, which emit a broad spectrum of wavelengths (Table 1).

Iron gall ink underdrawings, partly mixed with carbon-based black pigments, were identified by Dietz in 2015 in the panel paintings “Tree of Jesse” (Inv. No. HM 6) and “Bearing of the Cross” (Inv. No. HM 15) of the Frankfurt Dominican Altarpiece by Hans Holbein the Elder by means of SEM/EDX analysis on cross-sections [4] (p. 505–514). The panel painting “Virgin and Child” by Giovanni Battista Cima da Conegliano (Inv. No. 852) was selected because underdrawings with iron gall ink had been previously discovered in paintings by the Italian artist at the National Gallery London [1] (p. 31) and National Gallery of Scotland, Edinburgh [29] (p. 8).

### Analysis

The underdrawing of all three paintings was analysed by MA-XRF and LEDE-IRR. Data evaluation was accompanied by stereomicroscopy. Results were compared to invasive methods using SEM/EDX on cross-sections.

MA-XRF was performed using a Bruker M6 Jetstream [11], operated with a Rh-target X-ray tube at 50 kV and 600  $\mu$ A, equipped with a 30 mm<sup>2</sup> SDD spectrometer set to a maximum throughput of 275 kcps and collecting an energy range up to 40 keV. No filters were used for primary radiation. A beam size of 100  $\mu$ m was used for all

**Table 2** Varying measurement parameters of MA-XRF analysis chosen for different scans

Inv. No.	Scan	Localisation	Step size	Dwell time
HM 6	Overall 1–2	Lower part of the panel	375 $\mu$ m	25 ms/pixel
	Detail 1	Head of Jesse	305 $\mu$ m	3.04 <sup>a</sup> ms/pixel
	Detail 1	Head of Jesse	305 $\mu$ m	10 ms/pixel
	Detail 1	Head of Jesse	305 $\mu$ m	50 ms/pixel
	Detail 1	Head of Jesse	305 $\mu$ m	100 ms/pixel
	Detail 2	King David	305 $\mu$ m	250 ms/pixel
HM 15	Overall 1	Lower left part of the panel	375 $\mu$ m	25 ms/pixel
852	Overall 1	Overall	375 $\mu$ m	25 ms/pixel
	Detail 1	Dress of the Virgin	305 $\mu$ m	100 ms/pixel

<sup>a</sup> Fastest scan time possible

scans. Different acquisition parameters were employed due to the different requirements of the scans (Table 2). Dwell time was optimised to gain maximum intensity of sub-surface signals and trace elements. Overall scans were performed to study the elemental composition and its distribution, whereas detail scans were used to study the features of the underdrawing lines. In addition, a detail of the head of Jesse in Holbein the Elder's “Tree of Jesse” (Inv. No. HM 6) was selected to test the influence of the dwell time per pixel on the visibility of the underdrawing lines, starting with the fastest scan time possible up to a dwell time that allowed to show the underdrawing in detail. MA-XRF datasets were acquired, processed and evaluated using Bruker M6 software, datamuncher [30] and PyMca [31, 32].

IRR of the paintings by Holbein the Elder (Inv. No. HM 6, Inv. No. HM 15) were performed with an Osiris-A1 camera<sup>4</sup> [28], IRR of “Virgin and Child” by Cima da Conegliano (Inv. No. 852) with a vidicon tube system [33, 34].<sup>5</sup> Conventional IRR with a broad range of wavelengths using halogen-based Hedler<sup>®</sup> HT 19 s lights as excitation source were already existent.<sup>6</sup> IRR with five different narrow IR bandwidths at 880 nm, 940 nm, 1060 nm, 1330 nm and 1550 nm (Additional file 1: Suppl 1) was performed with IR-LED test lights for illumination in a dark room. These lights were built at the Steinbeis Transfer Centre at Aalen University and illuminate an area of 20.0  $\times$  40.0 cm, hence only details of the paintings

<sup>4</sup> Opus Instruments Ltd. The sensitivity of the InGaAs array is  $\lambda=900\text{--}1700$  nm [28].

<sup>5</sup> Hamamatsu Infrared Vidicon Camera C2741-03. The sensitivity of this vidicon tube system (PbO-PbS) ranges from 400 to 1800 nm (2200 nm) [35].

<sup>6</sup> The wavelength range of these lights could not be determined until now. Comparable Hedler H25s halogen lamps excite a wavelength range from  $\lambda=150\text{--}7500$  nm with  $\lambda_{\text{peak}}$  at 1250 nm [23] (p. 104).

could be studied [36]. For optical microscopy a Leica MZ 6 equipped with two Schott KL 1600 LED lights for visible light (VIS) was used. Cross-section analysis of the paintings by Holbein the Elder (Inv. No. HM 6, Inv. No. HM 15) were performed in 2015 by Dietz [4], whereas cross-sections of “Virgin and Child” by Cima da Conegliano (Inv. No. 852) were produced and analysed in the course of this study by first author. All microsamples were embedded in Technovit 2000 LC and grinded with Micro Mesh (granulation 1500–12000). Analysis of all cross-sections were performed with a polarised light microscope Leica (Leitz) DMR with a magnification of 500 for visible light (VIS) and ultraviolet (UV) illumination (filter set D, bandpass 355–425 nm). SEM/EDX was performed with a Zeiss EVO 60 VP, equipped with a XFlash 6130 SDD by Bruker for EDX analysis. All samples were carbon coated and analysed in high vacuum at 20 kV acceleration voltage, 150–200 pA current and 100 s measurement time with the distance between sample and detector ranging between 8.0 and 10.0 mm.

## Results

First results on the application of MA-XRF and LEDE-IRR on the analysis of iron gall ink underdrawings are presented in two case studies. The first study on paintings by Holbein the Elder focusses on possibilities and limits of visualising iron gall inks. The second case presents a detailed study of a beforehand unidentified and mainly invisible underdrawing of a panel painting by Cima da Conegliano.

### Hans Holbein the Elder “Tree of Jesse” (Inv. No. HM 6) and “Bearing of the Cross” (Inv. No. HM 15)

Hans Holbein the Elder (c. 1465–c. 1524) was a German painter active between Late Medieval and early Renaissance. Around 1500 he and his workshop, where he worked together with his workshop members including his brother Sigmund Holbein, created a couple of large and important altarpieces. Among these is the High Altarpiece of the Dominican Church in Frankfurt, painted in 1501 [37], whose art-technology was examined by Dietz in 2015 [4]. Today, eleven panels with an average size of 166.0 × 150.0 cm and the predella of the Frankfurt Dominican Altarpiece (76.3 × 277.5 cm) belong to the collection of the Städel Museum Frankfurt (Additional file 1: Suppl 3). Nine of these panel paintings were underdrawn with iron gall ink [4] (p. 505–514), which Dietz identified by studying optical features, conventional IRR and SEM/EDX analysis on cross-sections [4] (p. 138). The other three panel paintings were either not sampled or samples did not include an underdrawing layer. In all nine cases in which the material of the underdrawing could be studied both iron gall ink as well as carbon-based black

pigments could be detected. In six of the panel paintings iron gall ink and carbon black pigments were not only used separately, but also in mixture with each other [4] (p. 505–514). Hence it is not surprising, that the underdrawing could not be fully visualised by means of IRR with halogen lamps (Additional file 1: Suppl 4 and 5). Still, some of the lines invisible in IRR are accessible in visible light as they shine through overlying lead white painting layers [4] (p. 135), which likely became transparent due to the formation of lead soaps [38].

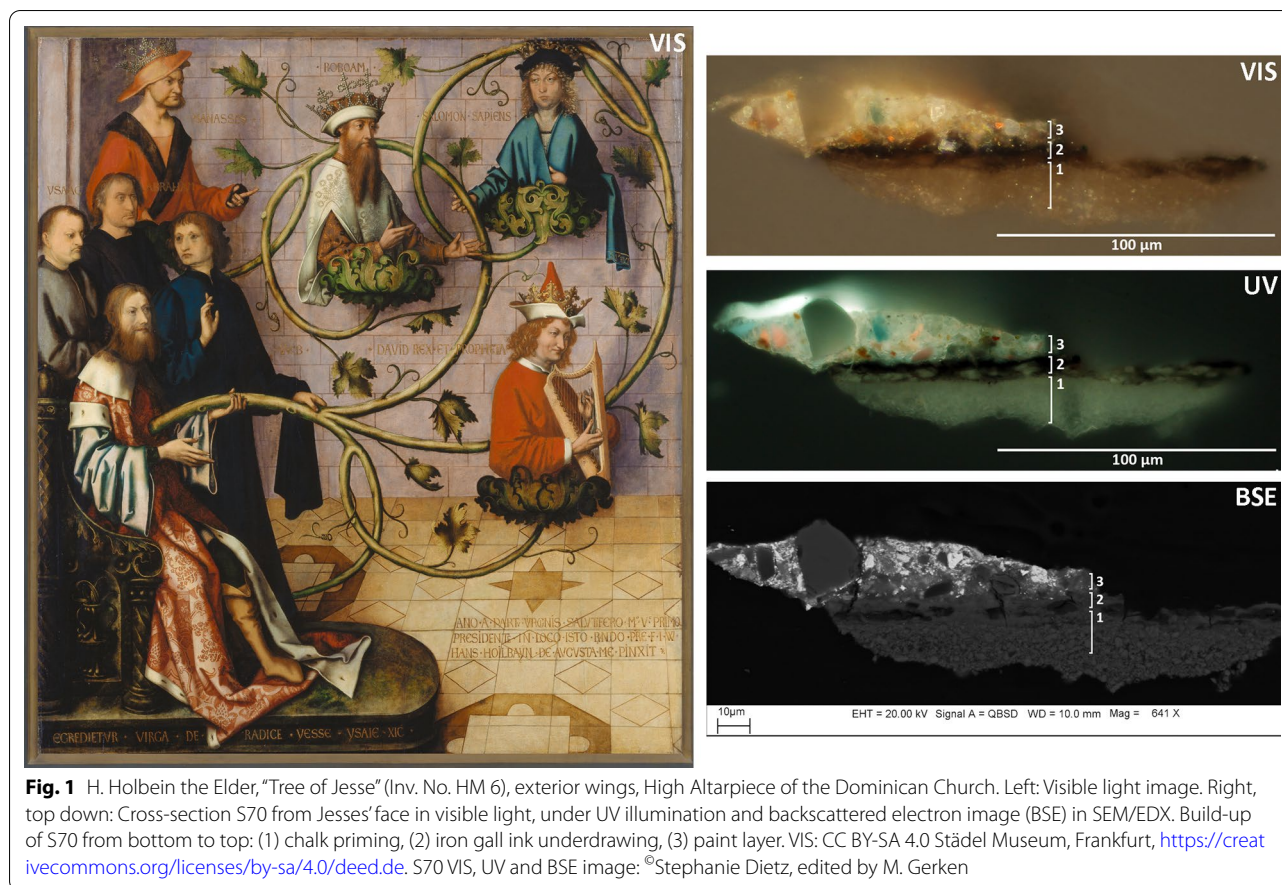
MA-XRF and LEDE-IRR were applied on two panels of the altarpiece in overall and detail scans. The lower part of the “Tree of Jesse” (Inv. No. HM 6) is located at the lower half on the exterior of the left outer wing of the retable (Fig. 1, VIS) and was (at least partly) underdrawn with pure iron gall ink (Fig. 1, right) [4] (p. 513).<sup>7</sup> In contrast, the panel “Bearing of the Cross” (Inv. No. HM 15) is part of the inner wings depicting the Passion of Christ, located on the lower left side. In areas accessible to MA-XRF scanning, iron gall ink was used in mixture with a carbon black pigment for compositional drawings [4] (p. 506).<sup>8</sup> Due to the limited accessibility of the large and heavy panel paintings, which are permanently on display, only lower parts of both panels could be examined (Additional file 1: Suppl 4, VIS and 5, VIS). MA-XRF detail scans were performed on Jesses’ head and King David’s harp, both located in lower parts of “Tree of Jesse” (Inv. No. HM 6) (Additional file 1: Suppl 4, VIS).

## Analysis

While Fe-K and Cu-K elemental maps of the MA-XRF overview scans (Fig. 2) are dominated by strong signals stemming from Fe- and Cu-rich pigments, which are present in the painting layers and conservation materials, the distribution of Mn-K is too noisy to show details, especially of sub-surface layers. Nonetheless, underdrawing lines become visible in large areas of the Zn-K distribution maps of both panel paintings (Fig. 2, red arrows), although Zn is also present in some of the copper green and blue pigments of the paint (Fig. 2, green arrows), e.g. in the green vines or the blue garment worn by Salomon located on the right side of Jesse. Yet, the course of the underdrawing lines as well as the ink’s fluid application are revealed by Zn-K elemental map. Fluid applied underdrawings, visible e.g. beneath the garment and head of Jesse or King David’s face and harp, show a consistent course of lines with smooth transitions from

<sup>7</sup> The exemplary sample S70 was removed from the incarnate of Jesses’ face at 63.0 cm from the upper edge and 23.1 cm from the left edge. The location of sample removal is mapped in Additional file 1: Suppl 4.

<sup>8</sup> For a better presentation, visual results on the latter (Inv. No. HM 15) can be found in the Additional file 1: Suppl 5 because they are highly comparable to results gained for Inv. No. HM 6.



**Fig. 1** H. Holbein the Elder, “Tree of Jesse” (Inv. No. HM 6), exterior wings, High Altarpiece of the Dominican Church. Left: Visible light image. Right, top down: Cross-section S70 from Jesse’s face in visible light, under UV illumination and backscattered electron image (BSE) in SEM/EDX. Build-up of S70 from bottom to top: (1) chalk priming, (2) iron gall ink underdrawing, (3) paint layer. VIS: CC BY-SA 4.0 Städel Museum, Frankfurt, <https://creativecommons.org/licenses/by-sa/4.0/deed.de>. S70 VIS, UV and BSE image: ©Stephanie Dietz, edited by M. Gerken

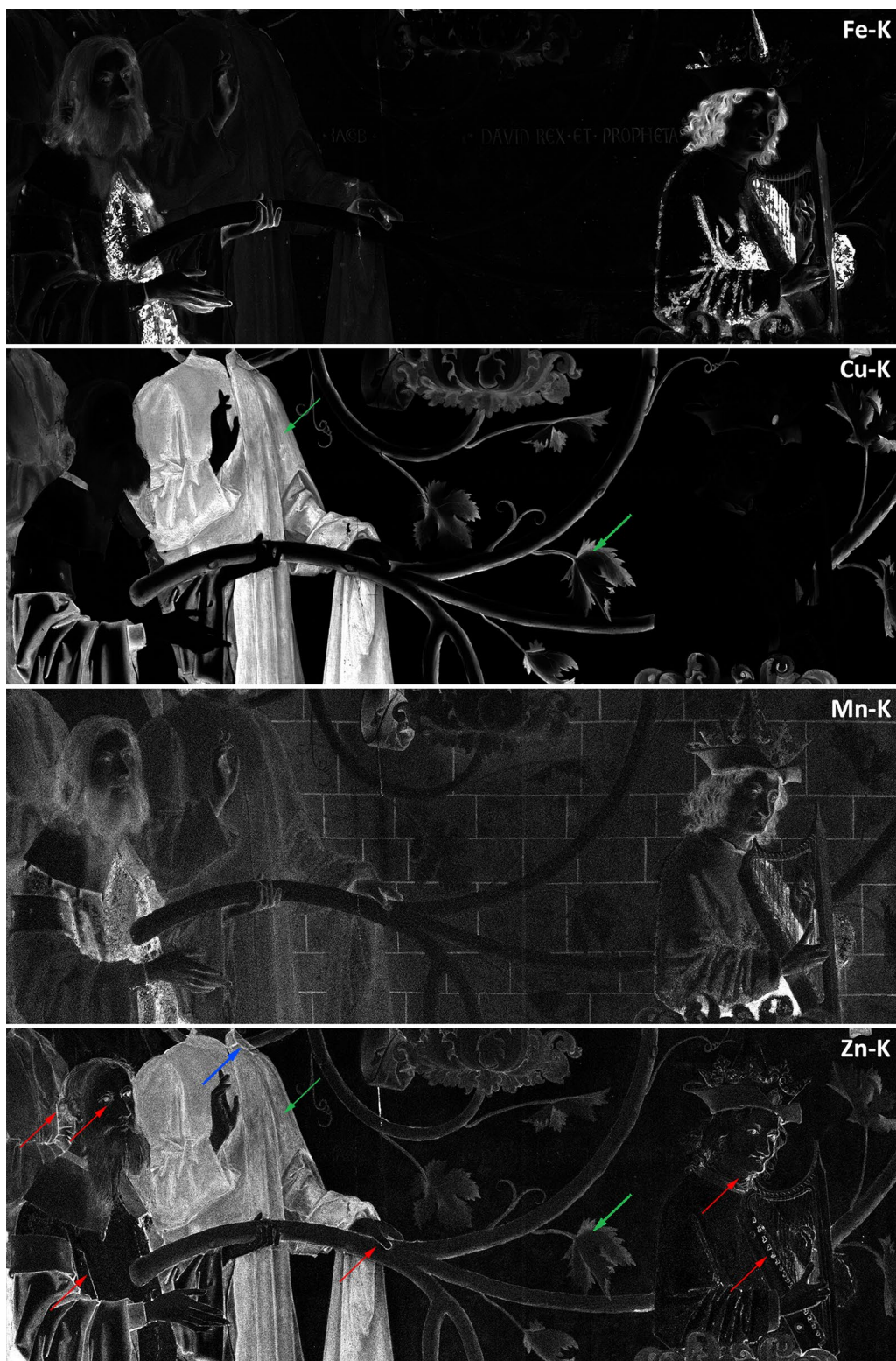
thickly to thinly applied areas and reveal traces of the application tool used, as e.g. brush or quill [39].<sup>9</sup> Furthermore, the Zn distribution reveals a *pentimento* in the left collar of Salomon’s blue garment, even though signals of the Zn-rich Cu-based pigment and Zn-rich underdrawing lines are partly overlapping (Fig. 2, blue arrow). The high amount of Zn within the underdrawing hints at the use of a Zn-rich material, which is consistent with the results by Dietz [4]. Subsurface underdrawing lines are apparent in the Zn-K distribution, no matter if the Zn-rich underdrawing was used pure (Inv. No. HM 6) or in mixture with a carbon black pigment (Inv. No. HM 15)<sup>10</sup> (Additional file 1: Suppl 5). The two detail scans of “Tree of Jesse” (Inv. No. HM 6) revealed properties and

application traces of the underdrawing in greater detail and contrast (Figs. 3, 4). The compositional lines visible in Zn-K maps not only roughly capture drapery of clothing and hair, but also indicate facial features in a more elaborate way with hatchings creating shadows and thin lines outlining wrinkles, a typical stylistic element of Holbein’s underdrawings [4] (p. 146–149). Besides thickly or thinly applied Zn-rich compositional lines, lines with low elemental signals could be identified, which could either hint at a high dilution or a mixture with another material.

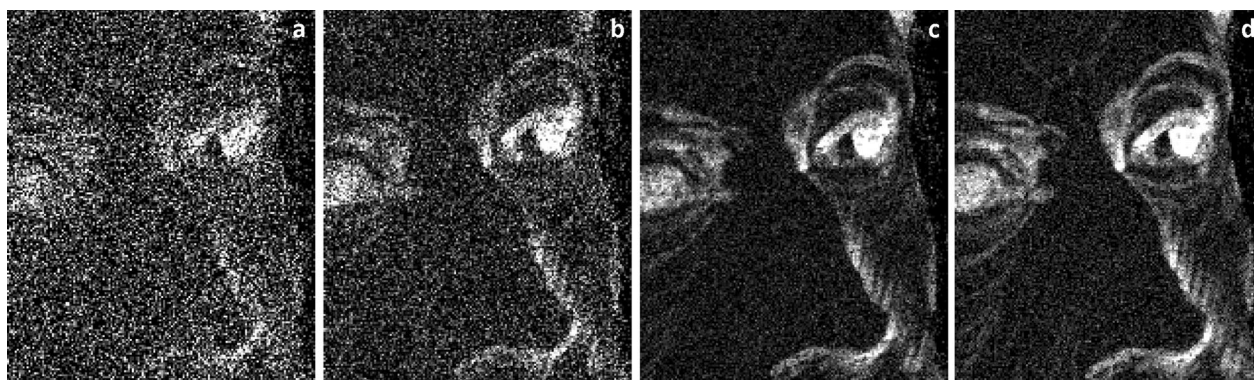
The visibility of the ink and its dependence on chosen MA-XRF parameters were tested in a detail scan of Jesse’s head, focusing on the dwell time per pixel. While overall scans were performed with a pixel size of 375 µm, details were scanned with a fixed pixel size of 305 µm to ensure the visibility of the underdrawing lines. In general, the step size should be chosen in accordance to the width of the underdrawing lines as well as the focus of research. In this case, a step size of 375 µm proved to be a good choice for visualising the overall distribution of the ink and was still sufficient to map large areas in a reasonable time (~24 h for 60.0 × 80.0 cm), whereas 305 µm proved sufficient for detail scans, which enabled characteristics

<sup>9</sup> Underdrawing lines of the Frankfurt Dominican Altarpiece mostly show application traces of different brushes. However, a few underdrawing lines on the predella of the altarpiece were likely applied with a quill [4] (p. 139–142).

<sup>10</sup> In “Bearing of the Cross” (Inv. No. HM 15) the underdrawings could be studied in five cross-sections (Additional file 1: Suppl. 5). In S11 and S14 iron gall ink mixed with a carbon black pigment could be identified as underdrawing material, whereas S13 and S18 solely contain iron gall ink and the underdrawing layer of S15 merely consists of a carbon black pigment (soot?) [4] (p. 506–507) (Additional file 1: Suppl 5).



**Fig. 2** H. Holbein the Elder, “Tree of Jesse” (Inv. No. HM 6), MA-XRF elemental maps of the lower part of the panel painting. The Fe-K, Cu-K and Mn-K distribution are dominated by the presence of Fe-, Cu- and Mn-rich pigments and conservation materials. The underdrawing becomes apparent in large parts of the Zn-K distribution map (red arrows), revealing a *pentimento* in the left collar of Salomon’s blue garment (blue arrow), although Zn is also present in Cu-containing pigments (green arrows). ©Städel Museum, Frankfurt am Main, Department for Art-Technology and Conservation of Paintings and Modern Sculpture, M. Gerken



**Fig. 3** H. Holbein the Elder “Tree of Jesse” (Inv. No. HM 6), detail of Jesse. MA-XRF Zn-K element map with differing dwell times: **a** 3.04 ms/pixel. **b** 10 ms/pixel. **c** 50 ms/pixel. **d** 100 ms/pixel. ©Städel Museum, Frankfurt am Main, Department for Art-Technology and Conservation of Paintings and Modern Sculpture, M. Gerken

of the ink application to be studied in detail. The dwell time was varied in four steps appropriate to a reasonable time exposure (Table 2). The tested variation of the chosen dwell time had a great impact on the visibility of the underdrawing. At fastest stage speed—in this case 3.04 ms/pixel—the presence of Zn could be determined, but signals could not be clearly linked to a specific distribution (Fig. 3a), while at 10 ms/pixel the course of underdrawing lines could already be seen in the Zn-K elemental map (Fig. 3b). At a dwell time of 50 ms/pixel characteristics like the fluid application of thick lines became apparent (Fig. 3c). With a dwell time of 100 ms/pixel thin lines with weak Zn-signals could be detected and visualised (Fig. 3d).

LEDE-IRR yielded heterogenous results. A varying mix of underdrawing lines could be distinguished in the head of Jesse. Only a few Zn-rich compositional lines were clearly visible at 1060 nm and transparent at 1300 nm. Most of the underdrawing could still be reported at 1550 nm with differing degrees of transparency. Furthermore, Zn-free lines became visible in IRR, which remained dark black equally to the irradiated IR wavelength. Apparently, Holbein used different materials for his composition simultaneously.

A second detail study of the underdrawing was carried out at King David’s harp (Fig. 4, VIS), which is depicted on the lower right side of “Tree of Jesse” (Inv. No. HM 6). A detail scan with a 250 ms/pixel dwell time proved successful in revealing parts of the underdrawing in the elemental distribution images of Fe and Cu. Again, the entire underdrawing with details of the application could only be visualised by Zn-K distribution (Fig. 4). However, correlation plots of Fe and Cu, Mn or Zn revealed the co-occurrence of all four elements (Fig. 4, bottom row). The comparison of elemental maps and correlation plots with

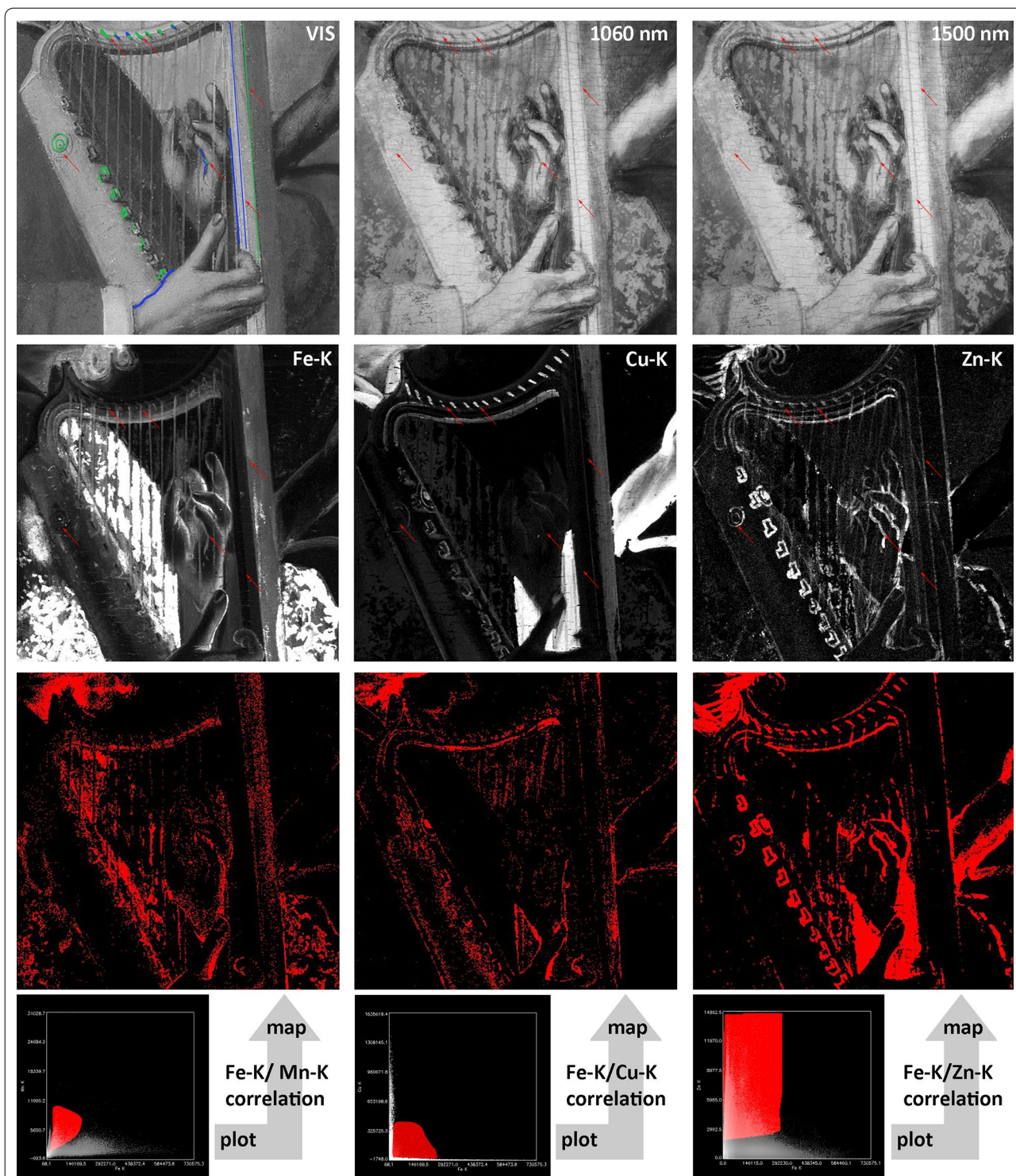
the VIS image shows, that Fe-, Cu-, Mn- and Zn-rich lines also seems to have been used for the final depiction of the harp’s structure and material, e.g. by indicating knotholes or the levers at the lower end of the strings.<sup>11</sup> LEDE-IRR also showed striking results. Although varying, most of the Zn-rich lines—no matter if apparent in VIS or completely covered by painting layers—grew transparent to a significant degree between 1060 and 1550 nm (Fig. 4, LEDE-IRR).<sup>12</sup> Nonetheless, a clear distinction became apparent between lines nearly invisible at 1550 nm (Fig. 4, VIS, green) and lines still clearly evident at 1550 nm (Fig. 4, VIS, blue). Elemental signals could be assigned to translucent brown lines, which do not include any pigment particles and are located either below a very thin light painting layer or upon the painting layer. While the brown lines situated between priming and paint layers can be clearly identified as underdrawing lines, the brown translucent lines integrated into the depiction appear to have been solely used in the harp. Both types show a remarkable fine pattern of broad drying cracks.

### Discussion

In the preliminary art-technological examination of the Frankfurt Dominican Altarpiece, Dietz could identify iron gall ink as underdrawing material in three cross-sections of the “Tree of Jesse” (Inv. No. HM 6) (Additional

<sup>11</sup> As these lines are part of the final depiction, questions arose whether the elemental signals derive from an iron gall ink or from a paint layer consisting of a copper-based pigment, that contains an impurity of Zn, with an admixture of an ochre pigment. In-depth evaluation of MA-XRF datasets could not clarify gained results and would require further analysis.

<sup>12</sup> The IR absorption properties in this case could be a source of error, because azurite and malachite, both Cu-based pigments, become likewise transparent between 1000 and 1300 nm [40], so that gained LEDE-IRR results could hint at different materials.



**Fig. 4** H. Holbein the Elder “Tree of Jesse” (Inv. No. HM 6). Top row, left to right: Visible light image of King David’s harp in greyscale with a mapping of underdrawing lines either visible (blue) or invisible (green) at 1550 nm, LEDE-IRR at 1060 nm and 1550 nm. Second row, left to right: MA-XRF element maps of Fe-K, Cu-K and Zn-K. Bottom rows, left to right: Mapping and plots of the correlation of Fe-K/Mn-K, Fe-K/Cu-K and Fe-K/ Zn-K. ©Städel Museum, Frankfurt am Main, Department for Art-Technology and Conservation of Paintings and Modern Sculpture, M. Gerken



file 1: Suppl 4, S69–S71) [4].<sup>13</sup> Two of these samples located in the head of Jesse could now be used as reference for interpreting Zn-rich underdrawing lines visible by means of MA-XRF as iron gall ink underdrawings. Comparable Zn-rich underdrawing lines assignable to iron gall ink became visible in all overview and detail scans by the Zn-K distribution of both examined panel paintings by Holbein the Elder (Inv. No. HM 6 and Inv. No. HM 15). In contrast to the Zn-K elemental images, the lines of the underdrawing remained only poorly visible or even completely invisible in the elemental maps of Fe, Cu or Mn, although an increased number of counts per second (cps) could be detected in the XRF spectra of underdrawn areas. The connection of all four elements could only be visualised by correlating elemental signals (Fig. 4, bottom row). Underdrawing lines became only partly visible within the Fe and Cu elemental maps of a detail scan of King David's harp, either due to the long dwell time of the scan or because some of these lines are only partly and thinly covered by painting layers. While the identification of Fe, Cu and Zn is consistent with previous SEM/EDX results, MA-XRF was also able to detect Mn. This further supports Dietz hypothesis, that a *vitriolum goslarensis* could be assumed for the production of the ink [4] (p. 138), as vitriols from this mining site contain approximately 9%  $\text{MnSO}_4$  [6] (p. 130). However, although the Rammelsberg in Goslar was apparently the largest production site for vitriol in Germany in the sixteenth century (e.g. in 1577, 250 tons were produced), from German pharmacy price lists (*taxae*) we know of other German mining sites of which the chemical composition of the vitriol is unknown [7].

As there are no Zn-based historical pigments before the nineteenth century, using Zn-K elemental maps for visualising iron gall inks firstly seems unsusceptible to error. Yet, vitriols – with or without Zn – were also used as additives to alter the properties of paints [41] (p. 42). Moreover, Zn is a common impurity in copper-based pigments [13] (p. 18), which is also apparent in the MA-XRF overall scans of “Tree of Jesse” (Inv. No. HM 6) (Fig. 2, green arrows). Therefore, the presence of a Cu-based pigment cannot be completely excluded if only MA-XRF results are considered. Due to overlapping reflectance properties of iron gall ink and Cu-based pigments like azurite or malachite, both materials cannot be clearly distinguished from each other by LEDE-IRR. Moreover, LEDE-IRR results in this case study varied strongly because the visibility of underdrawing lines is influenced by various parameters such as layer thickness and the admixtures of carbon-based black pigments. Nonetheless, the different reflectance properties of the underdrawing lines appear to be consistent with the differing

visibility of compositional lines in MA-XRF Zn-K distribution images, in which the visibility of the underdrawing lines varies in accordance with the amount of Zn present. Viz. lines with a high amount of Zn show an increased transparency between 1060 and 1550 nm (Fig. 4, VIS mapping, green), while lines with low Zn-K signals show little alteration (Fig. 4, VIS mapping, blue). The complexity of these results reflect the general material diversity of the Frankfurt altarpiece, which was underdrawn with different carbon black pigments, iron gall ink and various mixtures of both material groups [4] (p. 505–514).<sup>14</sup> The dark black lines visible in IRR and invisible in the Zn-K distribution images, e.g. in the head of Jesse (Additional file 1: Suppl 4, IRR), could indicate, that next to iron gall ink pure carbon-based black pigments were also in use for underdrawing the “Tree of Jesse” (Inv. No. HM 6). The complexity of the results presented as well as variations of quality and style of the underdrawing outlined before by Dietz [4] (p. 3) hint at a multi-stage composition process, that was partly executed directly on the panel. Dietz was furthermore able to prove that Holbein the Elder deliberately used underdrawing lines as part of his final depiction [4] (p. 3). It is therefore likely to deduce from the results of the MA-XRF detail scan of King David's harp, that iron gall ink could have been utilised within the painting process to partly characterise the wooden material and structure of the harp.

#### Giovanni Battista Cima da Conegliano “Virgin and Child” (Inv. No. 852)

Giovanni Battista Cima da Conegliano (c. 1459–c. 1517) was an Italian Renaissance painter who worked in Venice for most of his life. The panel painting “Virgin and Child” (1500–1501), belonging to the collection of the Städel Museum, shows a typical motif of the artist (Fig. 5, VIS). It was probably initially conceived for a full-figure altarpiece, but was later transformed into a half-figure format [42] (p. 136–137). Conventional IRR with a Vidicon (Fig. 5, IRR) revealed only few underdrawing lines [42] (p. 131).

#### Analysis

MA-XRF parameters (Table 1) were chosen in accordance with results gained from the examination of the panel paintings by Holbein the Elder (Additional file 1: Suppl 6). Again, an initial MA-XRF overall scan was able to reveal the presence of Zn in a noisy distribution that shows resemblance to the few underdrawing lines visible with conventional IRR (Fig. 5, IRR). To clarify results, a MA-XRF detail scan of the

<sup>13</sup> For Dietz results on “Bearing of the Cross” (Inv. No. HM 15), see note 10.

<sup>14</sup> Dietz could furthermore identify initial underdrawings executed with red chalk in the panel painting “Presentation in the Temple”, Frankfurter Dominikan altar, 1500–1501, mixed media on spruce, 167.0 × 151.2 cm, Hamburg, Hamburger Kunsthalle, Inv. No. HK-327 [4] (p. 132).



**Fig. 5** G. B. Cima da Conegliano, “Virgin and Child” (Inv. No. 852). Left: Visible light image. Right: Conventional IRR image (400–1800 nm). VIS ©Städel Museum, Frankfurt am Main, Foto: U. Edelmann. IRR ©Städel Museum, Frankfurt am Main

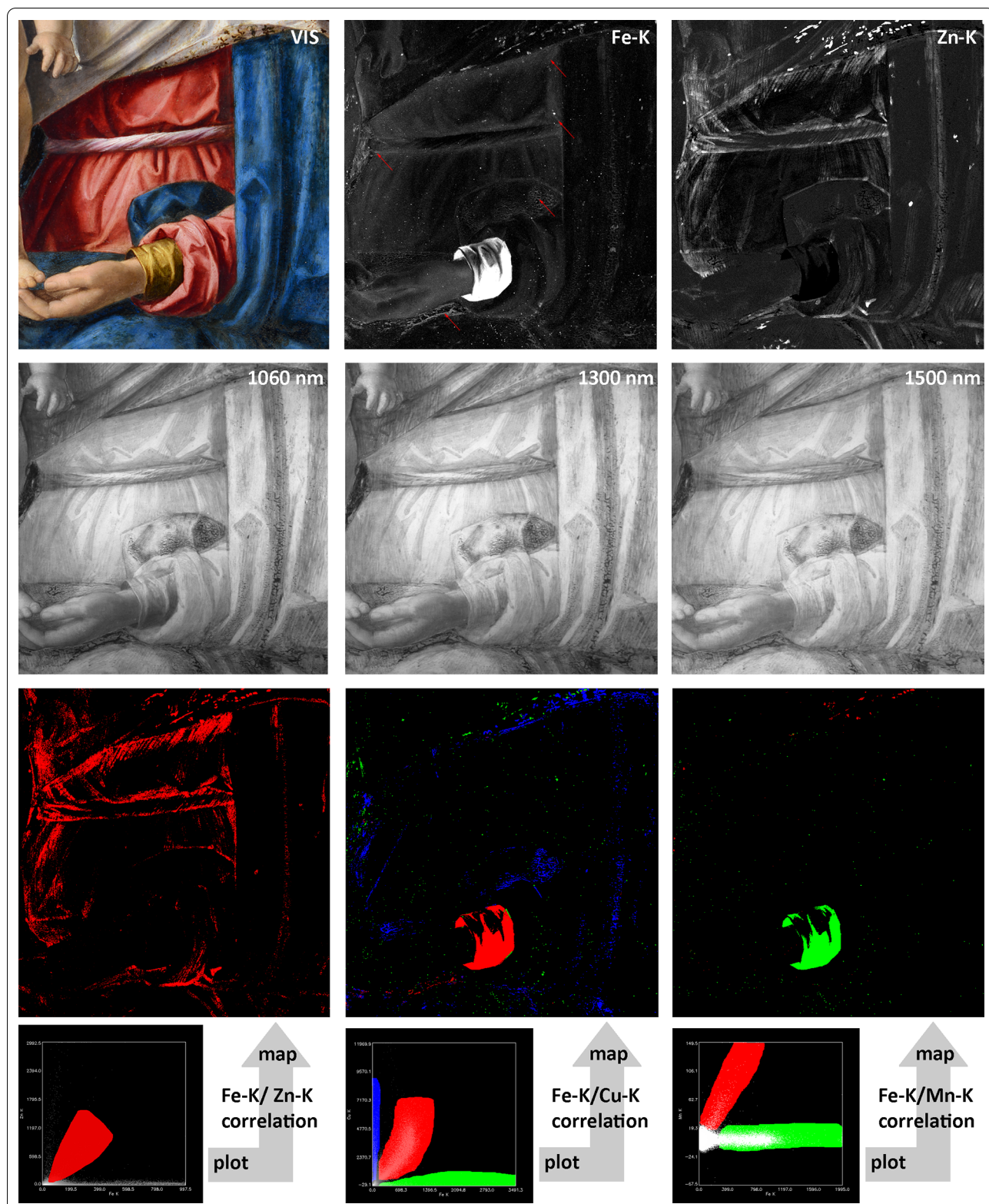
Virgin’s dress was performed (Fig. 6). Again, solely thickly applied strokes were visible in the elemental distribution of Fe (Fig. 6, Fe-K, red arrows), while the very detailed and complex underdrawing became apparent in total in the Zn-K elemental map (Fig. 6, Zn-K). The correlation plot of Fe and Zn indicate their co-occurrence within the underdrawing (Fig. 6, Fe-K/Zn-K correlation). In contrast to the underdrawing examined in the first case study, this underdrawing does not show a joint appearance of Fe and Cu or Mn, as evinced by their correlation plots (Fig. 6, Fe-K/Cu-K and Fe-K/Mn-K correlation). Furthermore, XRF spectra of underdrawn areas show a lower cps value of Cu and Mn. The MA-XRF detail scan revealed not only the fluid application, but also at least two different steps in the compositional planning. Firstly, the depicted scene appears to have been captured directly on the white gypsum<sup>15</sup> priming with a few thick sketchy lines that show characteristics of a reed pen. In a second step, details of the drapery and shadows were elaborated with finer lines and hatching, possibly applied with a brush and further washes (Fig. 6, Zn-K). In contrast to conventional IRR, underdrawing lines could be visualised more clearly with LEDE-IRR. Although visible with greater contrast at 1060 nm, all lines

are still apparent in varying degrees at 1300 nm or even 1550 nm (Fig. 6, LEDE-IRR).

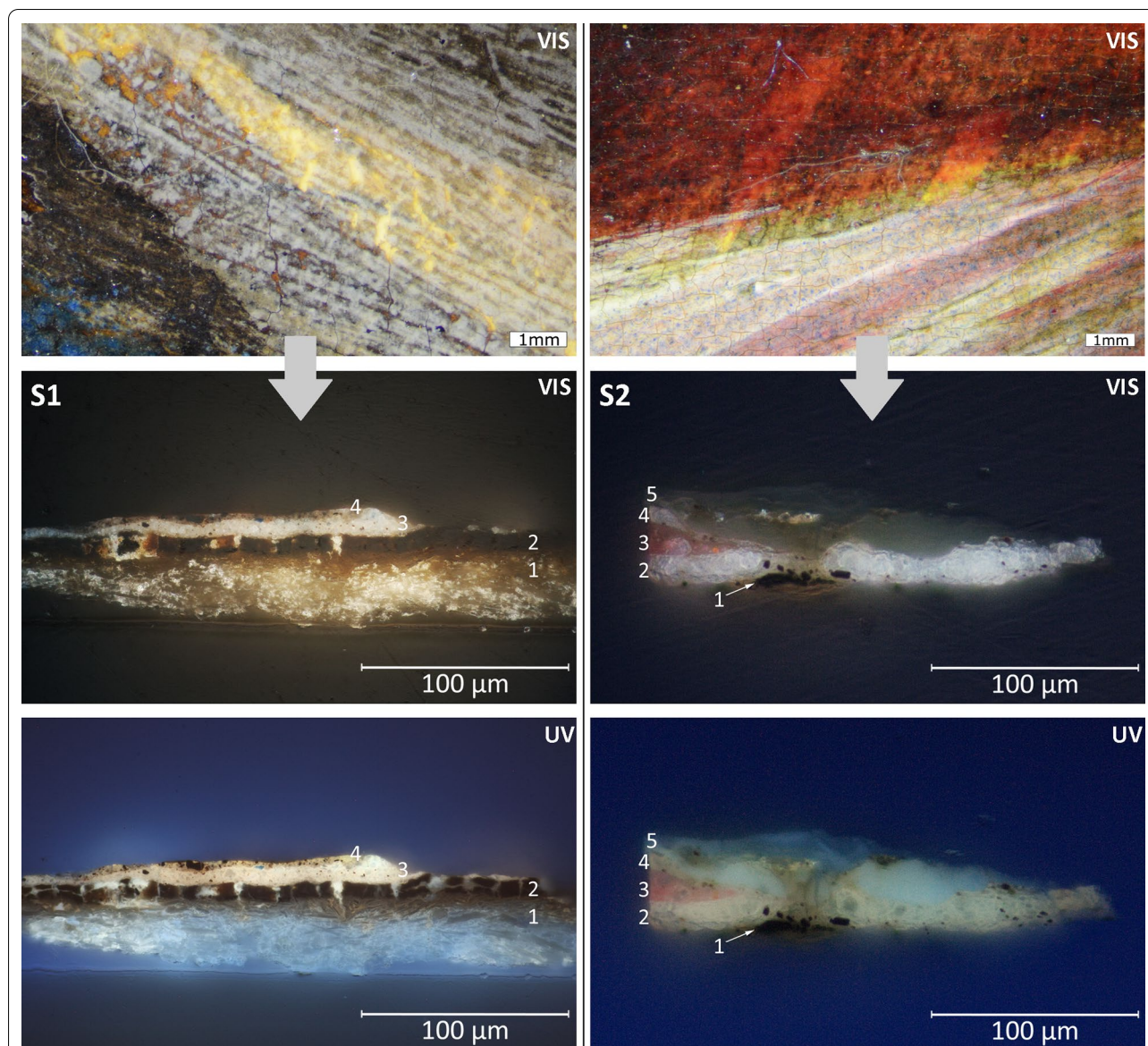
By stereomicroscopy two different types of underdrawing could be distinguished from each other (Fig. 7). Visual features of type 1 show translucent lines whose colour vary from light- to dark-brown depending on the thickness of the layer (Fig. 7, left). In thickly applied areas, a unique ageing pattern characterised by fine drying cracks becomes visible. In addition, paint layers covering dark brown lines appear to be damaged, too. Particularly blue areas, such as the Virgin’s dress, are shaped by thick drying cracks with a diameter up to 1 mm, in which the underlying brown underdrawing layer is revealed. In contrast, white or red painting layers are more stable and only show a pattern of very fine losses (< 1 mm), in which the underdrawing is either revealed or partly lost (Additional file 1: Suppl 6).<sup>16</sup> The aforementioned ageing pattern of the brown-black underdrawing becomes further apparent in dark field illumination of a cross-section sample

<sup>15</sup> Identified by SEM/EDX in the course of this study. The priming consists of large, acicular gypsum crystals, apparent in the backscattered electron (BSE) image of S1 (Additional file 1: Suppl. 6).

<sup>16</sup> In this study, typical damage symptoms of the ink and covering layers, as described by e.g. [3] (p. 76), are limited to areas, where the underdrawing has been applied thickly or overlying paint layers contain blue pigments (Additional file 1: Suppl. 6). Hence, this ageing pattern does not necessarily appear when an iron gall ink has been used, as in large areas of the Frankfurt Dominican Altarpiece, and might be dependent on the recipe used for the production of the ink [4] (p. 134), or other reasons.



**Fig. 6** G. B. Cima da Conegliano “Virgin and Child” (Inv. No. 852). Top row, left to right: Visible light image of the Madonna’s dress, MA-XRF element maps of Fe-K and Zn-K. Second row, left to right: LEDE-IRR at 1060 nm, 1300 nm and 1550 nm. Bottom rows, left to right: Mapping and plots of the correlation of Fe-K/Zn-K, Fe-K/Cu-K and Fe-K/Mn-K. ©Städel Museum, Frankfurt am Main, Department for Art-Technology and Conservation of Paintings and Modern Sculpture, M. Gerken



**Fig. 7** G. B. Cima da Conegliano “Virgin and Child” (Inv. No. 852). Left, top down: Microscopic image of the brown translucent underdrawing type 1, related cross-section S1 under visible light and UV illumination. Build-up of S1 from bottom to top: (1) gypsum priming, (2) underdrawing, (3) light grey paint layer, (4) grey paint layer. Right, top down: Microscopic image of underdrawing type 2 beneath the cord of the Virgin’s dress and associated cross-section S2 under visible light and UV illumination. Build-up of S2 from bottom to top: (1) underdrawing, (2) white paint layer, (3) red paint layer, (4) varnish, (5) retouching. ©Städel Museum, Frankfurt am Main, Department for Art-Technology and Conservation of Paintings and Modern Sculpture, M. Gerken

taking from a thickly applied composing line, as the dark translucent layer is divided by drying cracks every 20–50 µm (Fig. 7, S1, VIS).<sup>17</sup> When exposing micro-samples to UV radiation (Fig. 7, S1, UV) the underdrawing appears black. By means of SEM/EDX analysis, Fe, Zn, Al, K, Mg and S could be identified within the underdrawing layer, indicating the

<sup>17</sup> Sample S1 was removed from the collar of the Virgin at  $x=37.9$  cm and  $y=47.6$  cm, measured from the lower left corner. The location of sample removal is mapped in Additional file 1: Suppl. 6.

usage of iron gall ink (Additional file 1: Suppl 6). Moreover, SEM/EDX analysis of the underdrawing layer indicate that another organic component was admixed to the iron gall ink.<sup>18</sup>

By stereomicroscopy, type 2 could solely be determined below the light violet cord of the Virgin’s dress (Fig. 7, right). While appearing to be of green colour under the

<sup>18</sup> This can be presumed as the underdrawing layer melted in high vacuum during SEM/EDX.

stereomicroscope, cross-section reveals a particle-rich thin black layer (Fig. 7, S2).<sup>19</sup> In contrast to the brownish underdrawing lines, this type of underdrawing remains slightly darker when excited with 1550 nm. By means of SEM/EDX, Fe, Zn, Al, K, Mg and S (as well as traces of Cu) could be identified within the underdrawing layer (Additional file 1: Suppl 6), hinting at the use of an iron gall ink. Moreover, dark black particles embedded within the underdrawing layer (Fig. 7, S2, VIS) indicate the admixture of a carbon black pigment, which could not be further specified by means of SEM/EDX and could cause the increased visibility of these underdrawing lines at 1550 nm.

### Discussion

By identifying the joint occurrence of Fe, Zn, Al, K, Mg and S, SEM/EDX results of both types of underdrawing of the “Virgin and Child” (Inv. No. 852) indicate the presence of an iron gall ink, used both pure and in mixture with a carbon black pigment. Properties of the underdrawing examined by further analytical techniques such as MA-XRF, stereomicroscopy and cross-section analysis are likewise characteristic for iron gall inks. The co-occurrence of Fe and Zn within the whole underdrawing (Fig. 6, Fe-K/Zn-K correlation) as well as visual properties studied by stereomicroscopy—especially the ink’s colour, translucency and typical ageing pattern—were indispensable for interpretation of analytical results. The high amount of Zn detected by means of MA-XRF and SEM/EDX could indicate the use of a vitriol from a Zn-rich extraction site for the production of the ink. Solely IR reflectance properties studied by LEDE-IRR were not very significant, as the underdrawing remained visible at 1550 nm, which could be due to either its thick application (Fig. 7, left) or the admixture of a carbon black pigment (Fig. 7, right).

Published art-technological results of other paintings by Giovanni Battista Cima da Conegliano describe a comparable use of different materials. In the underdrawing of the unfinished painting “Virgin and Child with S. Andrew and S. Peter” at the National Gallery Scotland (Inv. No. 1190), a small amount of carbon black pigment particles could be identified within the iron gall ink underdrawing. This could either indicate the mixture of both materials or, as Dunkerton and Roy concluded, a preliminary drawing executed with charcoal that was afterwards redrawn with an iron gall ink, as recommended in Cennino Cennini’s famous tract “Il Libro dell’Arte” written around 1390 [29] (p. 8) [43]. Moreover,

uncovered underdrawing lines of this unfinished painting show characteristics both of a quill and a brush, which is well in accordance with quill traces identified within the Zn elemental distribution map of the Städel’s painting. Iron gall ink could also be determined in the underdrawing of Cima da Conegliano’s “Incredulity of St. Thomas”, painted between 1502 and 1504, at the National Gallery London (Inv. No. NG 816) [1] (p. 31). Carbon black pigment underdrawings have been detected in further panel paintings by Cima da Conegliano, such as the “Pala” from 1492, part of the high altarpiece of the cathedral of Conegliano, by cross-section analysis [44] (p. 36).

Formerly believed to be underdrawn with only a few lines and an unidentified fluid applied material, the recent examination of Cima da Conegliano’s “Virgin and Child” (Inv. No. 852) was not only able to visualise the complex and detailed underdrawing throughout the painting, but could indicate the use of a Zn-rich iron gall ink.

### Conclusions

The presented case studies outline possibilities and limits of the non-invasive analysis of iron gall ink underdrawings, used either pure or in mixture with carbon-based black pigments, by means of MA-XRF and LEDE-IRR. Generally, in all three cases the underdrawing could be deliberately studied and visualised in its overall application, characteristics and style by the applied analytical approach.

In all cases, Zn signals deriving from a vitriol with a high amount of ZnSO<sub>4</sub> were essential for MA-XRF mapping, not only to visualise underdrawing lines, but also for material characterisation. The potential invisibility of an iron gall ink underdrawing in the Fe, Cu and Mn distribution could be a major issue if a Zn-free vitriol was used for the ink’s production. As shown in the case of the “Tree of Jesse” by Holbein the Elder (Inv. No. HM 6), this problem could be partly solved by using correlation plots (Fig. 4, bottom row). Furthermore, this paper presented a novel application of IRR using narrow IR bandwidths for illumination (LEDE-IRR) to study IR reflectance properties of underdrawings. LEDE-IRR was able to distinguish between different types of underdrawings in panel paintings by Holbein the Elder (Fig. 4, top row), whereas results were not significant in the second case study on Cima da Conegliano’s “Virgin and Child” (Fig. 6, second row). As IR reflectance properties are dependent on various determinants, gained results are not unequivocal. Yet, although LEDE-IRR did not allow to clearly distinguish between different materials in the presented cases, it is able to provide images of underdrawings regardless of their composition, that could not be visualised before by means of conventional IRR. Nonetheless, results of both analytical techniques have to be interpreted cautiously,

<sup>19</sup> The thin layer probably only appears to be green due to the surrounding red paint layers. Sample S2 was removed from the cord of the Virgin’s dress at  $x=36.9$  cm and  $y=28.2$  cm, measured from the lower left corner. The location of sample removal is mapped in Additional file 1: Suppl. 6.

**Table 3** Overview about gained results

Object	Microscopy	MA-XRF	LEDE-IRR	SEM/EDX
Holbein the Elder “Tree of Jesse” (Inv. No. HM 6)	Brown-black, translucent, no particles visible	Fe, Cu, Zn	Lines with varying properties, either invisible or clearly visible at 1550 nm	Fe, Cu, Zn, Al
Holbein the Elder “Bearing of the Cross” (Inv. No. HM 15)	Brown-black, translucent, black particles visible	Fe, Cu, Zn	Visible up to 1550 nm with only a slightly enhanced transparency	Fe, Cu, Zn, Al
Cima da Conegliano “Virgin and Child” (Inv. No. 852)	Type 1: Brown-black, translucent, no particles visible. Fine drying cracks in thickly applied strokes	Fe, Zn	Visible up to 1550 nm with only a slightly enhanced transparency	Fe, Zn, Al, K, Mg, S
	Type 2: Green(?) / black, thinly applied lines containing a noticeable amount of black particles	Fe, Zn	Visible up to 1550 nm	Fe, Zn, Al, K, Mg, S, (Cu)

because Cu- and Zn-containing materials with similar characteristics such as vitriol and verdigris were likely utilised in sixteenth century paintings to modify paint properties [41, 45], as e.g. in coloured inks by Hans Holbein the Elder [4] (p. 137). Hence, in all cases microscopy and SEM/EDX on cross-sections proved crucial for interpretation of gained results. In general, the outcomes of this study prove, that only by combining different analytical and post-processing methods with microscopical observations, a final conclusion on an underdrawing material can be drawn (Table 3).

By visualising these formerly partly invisible underdrawings, a new access for further studies with wider application possibilities is created – overhauling a system, in which the material of an underdrawing material could only be examined in case studies, which required the removal of micro-samples and their analysis by techniques, that are only limitedly accessible. The presented approach enables the study of the whole underdrawing and not merely a selected point that might not be representative for the entire object. Furthermore it promotes interdisciplinary exchange as the gained results are readily accessible to disciplines without deep knowledge in natural sciences, as e.g. art-historians. Moreover, results can be more easily used for art education of the general public.

## Outlook

Iron gall ink is commonly thought to have been used only rarely for underdrawing paintings. Considering that this is solely assumed because non-carbon-based underdrawings poorly register in conventional IRR and invasive analysis is only applied in single in-depth studies on individual paintings, the results presented in this article could hint at a much broader use in Italy and Germany around 1500. A broad application of this novel non-invasive analytical approach could therefore expand knowledge on non-carbon-based underdrawings and overturn current beliefs. However, a more detailed evaluation

of the possibilities and limits of the analysis of different iron gall inks requires further research on test specimens, which is currently being conducted at the Städel Museum Frankfurt. Further unidentified components of the underdrawing of Cima da Conegliano’s “Virgin and Child” (Inv. No. 852) will be analysed by additional analysis such as Fourier transform infrared spectroscopy with focal plane array imaging (FTIR/FPA) on the presented cross-sections. Some of the depicted portraits of the Frankfurt Dominican Altarpiece by Holbein the Elder are based on portrait studies, that were beforehand drawn on paper by the artist, such as a Dominican monk [46] (p. 222). Technology and style of the portraits’ underdrawings will be compared to new results on the material and execution of the portrait studies on paper [47] (p. 56).

## Abbreviations

BSE: Backscattered electron image; FTIR/FPA: Fourier transform infrared spectroscopy with focal plane array imaging; IR: Infrared radiation; IRR: Infrared reflectography; LEDE-IRR: LED-excited infrared reflectography; MA-XRF: Micro-X-ray fluorescence scanning; nm: Wavelength; P-XRF: Point X-ray fluorescence analysis; SEM/EDX: Scanning electron microscopy with energy dispersive X-ray micro-analysis; VIS: Visible light image; XRR: X-ray radiography.

## Supplementary Information

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**Additional file 1.** Supplementary material.

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#### Author contributions

MG wrote the manuscript which was revised by JS and CK. MA-XRF scanning and data evaluation and LEDE-IRR of all paintings as well as cross section and SEM/EDX analysis of Inv. No. 852, MG; cross-section and SEM/EDX results of the paintings by Holbein the Elder were kindly provided by Stephanie Dietz. All authors have read and approved the manuscript.

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#### Availability of data and materials

The datasets generated and analysed during the current study are not publicly available as they are being further evaluated for the doctoral thesis of the corresponding author but are available from the corresponding author on reasonable request.

#### Declarations

#### Competing interests

The authors declare that they have no competing interests.

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