

# **Florentine papyri under examination: the material study of the inks used at the beginning of the Common Era in the “Family of Kôm Kâssûm” Archive (Hermopolis)**

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**Abstract:** Carbon inks with metallic admixtures are found on some papyri of the 2nd century CE from a family archive in Hermopolis. The great diversity of inks found in a single household within a short period of time suggests that inks were purchased rather than self-made.

**Keywords:** carbon ink, iron-gall ink, mixed ink, XRF ink analysis, family archives, Hermopolis

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## **Introduction**

The term carbon ink refers to a suspension of carbon particles in the form of soot or charcoal in an aqueous-soluble binder. This type of ink has been in use everywhere since Antiquity, and its existence in Egyptian, Greco-Roman and medieval times is widely documented in literature.<sup>1</sup> Nowadays

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<sup>1</sup> Lucas 1922; Lee/Quirke 2000:108.

this type of ink, commercially known as China ink, is still very popular in drawing and calligraphy.

Scientific analyses have often reported the use of pure carbon ink in Greco-Roman Egypt.<sup>2</sup> Besides pure carbon inks, evidence of carbon inks containing metal has been unveiled from the Greco-Roman period onwards. This is the case for a charred fragment from Herculaneum, whose carbon ink was found to contain lead in a quantity that far exceeds trace amounts (Paris, Institut de France).<sup>3</sup> Similarly, a number of the Dead Sea Scrolls, among them the famous Genesis Apocryphon (1Q20 [TM 397641]) were penned with carbon ink that contains an amount of copper large enough to cause almost complete disintegration of the skin-based materials of the scroll.<sup>4</sup> A considerable amount of copper found in soot ink can be associated with the detailed ink recipe offered by the 1st century CE Greek physician Dioscorides, who suggests adding a copper-based substance (*chalcanthon*) to soot for antibacterial purposes.<sup>5</sup> In contrast, a study on some fragments kept in the Carlsberg Collection (Copenhagen) and coming from Pathyris (the archive of Horos son of Nechouthes [TM Arch id 106]) and Tebtunis (Temple Library [TM Arch id 537]) found a small amount of copper in the form of cuprite, azurite and malachite in the ink used for writing. The authors interpreted their finding as an indication of the use of glassmakers' soot in the manufacturing of the ink.<sup>6</sup> This would correspond well with the information provided by the same Dioscorides, who mentions this type of soot as the best one to be used for painting.<sup>7</sup> This last finding suggests that the trace amount of metals in carbon inks was not always the product of the intentional introduction of metallic salts in the mixture resulting in what it is nowadays sometimes called a "mixed ink".<sup>8</sup>

The black insoluble pigment of iron-gall ink, iron gallate, is obtained from the chemical reaction between gallic acid and ferrous iron. Historically, the first reactant was often introduced in the form of gallnut

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<sup>2</sup> Ghigo/Torallas Tovar 2020; Bonnerot et al. 2020.

<sup>3</sup> Brun et al. 2016. The fragment was contained in a box called "Objet 59" that the King of Naples gave Napoleon Bonaparte as a gift in 1802. See also Bonnerot et al. 2020.

<sup>4</sup> Nir-El/Broshi 1996.

<sup>5</sup> Dioscorides, *De materia medica* V 161.

<sup>6</sup> Christiansen et al. 2017; Christiansen 2017.

<sup>7</sup> Dioscorides, *De materia medica* V 162.

<sup>8</sup> Strictly speaking, mixed inks belong to a category of inks obtained by blending carbon inks with plant or iron-gall inks.

extract, whereas the second one was commonly extracted from vitriol, a mixture of metal sulphates. It is noteworthy that a single component of vitriol, iron (II) sulphate or green vitriol, reacts with gallic acid to produce a black precipitate. It seems to us that this circumstance was not immediately perceived, and some inks would contain copper rather than iron, which led to the appearance of an ambiguous term: metal-gall ink<sup>9</sup>. The first analytic evidence for iron-gall ink we have so far in Greco-Roman Egypt comes from a Book of Proverbs dating to the 4<sup>th</sup> century (Berlin, Saatsbibliothek, Ms. Orient. Oct. 987 [TM 107968]),<sup>10</sup> while the first written recipe is probably recorded in PGM XII [TM 55954], where gallnuts are mixed with *misý* and *chalcanthon*.<sup>11</sup> It must be stressed, though, that without unequivocal identification of the chemical compounds named *chalchanton* and *misý* in Antiquity, the association of this recipe with iron-gall ink should be treated as tentative. In any case, it should not be forgotten that the reaction at the base of iron-gall ink may have been already empirically known three centuries before the Common Era. At that time, Philo of Byzantium used a mixture of water and *chalcanthon* to make a text reappear that had been previously written on leather with gallnut extract, resulting in an invisible trace.<sup>12</sup>

Modern research has often attempted to determine the exact chemical composition of these substances, basing its arguments either on the etymology (e.g.: in Greek *chalcos* means copper) or on their chemical properties.<sup>13</sup> While it is quite clear that in the Middle Ages *chalcanthon* was the name for blue vitriol (copper (II) sulphate), its exact chemical composition in Antiquity cannot be unequivocally identified. Analytical evidence obtained on black writing inks revealed that significant amounts of copper were present in the Greek signatures of some bilingual documents dating to the last centuries before the Common Era. Interestingly, the demotic text on these same documents was penned using carbon ink (Paris, Musée du Louvre, N 2433, N 2416, N 2410, N 2422 [TM 44209; TM 3567; TM 3570; TM 7141]).<sup>14</sup> Similarly, an increased level of copper was recently detected in one of the inks of a papyrus roll written in Theadelphia

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<sup>9</sup> Aceto et al. 2008.

<sup>10</sup> Ghigo et al. 2018.

<sup>11</sup> PGM XII 399 (Preisendanz 1931:83).

<sup>12</sup> Philo of Byzantium, *Mechanike Syntaxis* V 77. Philo uses the expression *chalcou de anthous* (literally: flower of copper).

<sup>13</sup> Karpenko/Norris 2002; Zerdoun Bat-Yehuda 1983:80; Bailey 1932:175,178–9.

<sup>14</sup> Delange et al. 1990.

(Fayum) during the reign of Hadrian (Florence, P.Laur. inv. 19655 [TM 700838–700840]).<sup>15</sup> Given that it also contains carbon, one could tentatively associate this ink with Dioscorides’ recipe mentioned above.<sup>16</sup> On the other hand, the brown halos around the characters seem to indicate that the ink might have contained tannins in addition to soot and a copper-based substance. Such an ink could be attributed to the category of mixed carbon/iron-gall ink, in which copper substituted for iron. Recent analysis of the documents dated to the 4<sup>th</sup> – 3<sup>rd</sup> century BCE and inscribed with exactly this type of ink places the beginning of the transition from the carbon to iron-gall ink into the early Hellenistic time.<sup>17</sup>

The analytical and written evidence suggests that the centuries around the beginning of the Common Era were a crucial period in the technological evolution of writing media: the intentional addition of metallic salts to carbon ink may have been a first step towards the establishment of iron-gall inks. Trying to collect further analytical data on this transition period, this work presents the archaeometric study of a group of papyri found in 1903 during Italian excavations in the Kôm Kâssoum, at Hermopolis.<sup>18</sup> The papyri were found in a niche in a house, where they were intentionally stored by their owners (a wealthy family whose members held important positions in public administration). This family archive, now split between the Biblioteca Medicea Laurenziana and the Istituto Papirologico “G. Vitelli” (Florence), consists of nearly a hundred fragments of various dimensions, many of them still unpublished: they are mostly accounts, receipts and contracts.<sup>19</sup> Among the published texts, the dated ones cover the years between AD 60 and the reign of Trajan.<sup>20</sup> Besides dating to a crucial period for the analysis of ink composition, this archive also offers the interesting opportunity to compare inks used by the

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<sup>15</sup> Rabin/Wintermann/Hahn 2019.

<sup>16</sup> Dioscorides, *De materia medica* V 162.

<sup>17</sup> Nehring et al, 2021.

<sup>18</sup> Breccia 1903. Breccia 1905.

<sup>19</sup> Messeri/Pintaudi 2000:265. Messeri/López García 2019. TM Arch id 555.

<sup>20</sup> The latest date recorded in a document certainly belonging to the archive (PSI inv. 4317 [TM 828869]) is AD 113/114. The date AD 125 appears in a papyrus (PSI VII 788) that, although probably found during the excavations in Hermopolis, may actually not belong to this specific group (as shown by its physical features). It is therefore to be marked as uncertain in the lists provided by Pintaudi 1998–99:244, Messeri/López García 2019:64, and TM Arch 555.

same persons and in the same household.<sup>21</sup> Scholars identified several handwritings, and some of them can be attributed to well-known members of the family. For this study, we selected 15 papyri, with the aim (1) to cover a good number of different (but chronologically and geographically homogeneous) handwritings and (2) to analyse different texts written by the same persons (in particular, by two brothers with the same name: Eudaimon the Elder and Eudaimon the Younger).<sup>22</sup> The results presented below show that conventional carbon inks were used in only about half of the texts analysed in this work; this finding stresses the necessity for routine technical inspection of manuscripts containing black writing media. In addition, the limitations imposed by the conservation state of the archaeological material and by the analytical instruments used while working on site will be pointed out.

### Experimental part

Our standard protocol for ink analysis consists of a primary screening to determine the type of ink and a subsequent in-depth analysis using several spectroscopic techniques: XRF, FTIR and Raman.<sup>23</sup>

The primary screening is carried out by means of near-infrared reflectography. Optical differences between carbon, plant and iron-gall inks are best recognized by comparing their response to infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1400 nm and plant ink disappears at ca. 750 nm.<sup>24</sup> The in-depth investigation includes XRF analysis to determine the contribution of the inorganic components of the ink. In the case of vitriolic iron-gall inks, we establish their fingerprints, i.e. the characteristic ratios of the minor metallic components of the ink to its major component, iron.<sup>25</sup> Unfortunately, the inherent heterogeneity of papyrus and the often poor conservation state of the writing media frequently prevent the use of the fingerprint model.<sup>26</sup> Time

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<sup>21</sup> Messeri 2009. The attributions for the still unpublished papyri are proposed here for the first time: we want to thank Gabriella Messeri for suggestions on this matter.

<sup>22</sup> Nos. 3 and 4 in the family tree provided by Messeri 2009:246.

<sup>23</sup> Rabin et al. 2012.

<sup>24</sup> In their study, Mrusek/Fuchs/Oltrogge 1995 indicate that iron-gall ink becomes transparent at 1200 nm. However, our recent tests using an IR camera showed that fresh iron-gall ink becomes completely transparent at longer wavelengths.

<sup>25</sup> Hahn et al. 2004; Rabin et al. 2012.

<sup>26</sup> Ghigo/Rabin/Buzi 2020.

constraints precluded the use of Raman and FTIR spectroscopy in this study.

### ***DinoLite USB microscope, AD413T-I2V***

This small USB microscope is only 10 cm in size, and it is equipped with three different light sources: near-infrared (940nm), UV (395 nm) and a white LED light (external). Comparing the VIS image with the corresponding near-infrared one, we determine the ink typology by observing the changes in the opacity of the ink. At 940 nm, carbon-based inks show no change in opacity, while the opacity of iron-gall inks changes considerably, and plant inks become transparent. Since the optical behaviour of the ink is determined by the main component, this simplified version of NIR reflectography is not always suited for the recognition of mixed inks. When no change of opacity is observed, the ink contains a substantial amount of elemental carbon that masks other possible components.

### ***Elio Bruker Nano GmbH (formerly XG Lab)***

This X-ray spectrometer features a 4W low-power rhodium tube, adjustable excitation parameters and a 25 mm<sup>2</sup> SDD detector with energy resolution <140 eV for Mn K $\alpha$ . With its beam spot of ca. 1 mm, it was used to collect data as a single measurement at operating conditions of 40kV and 80 $\mu$ A, with an acquisition time of 2 minutes. Peak fitting and semi-quantitative data evaluation were conducted using Bruker's SPEKTRA software.

### ***ArtTAX 800 Bruker Nano GmbH***

ArtTAX is a micro-X-ray spectrometer well known in the field of cultural heritage and belongs to the standard equipment of many large museums. It features a low-power, air-cooled molybdenum X-ray tube, polycapillary optics resulting in a beam spot of about 70  $\mu$ m diameter, a CCD camera for sample positioning and an electrothermally cooled Xflash detector (SDD, area: 30 mm<sup>2</sup>) with an energy resolution of <150 eV for Mn K $\alpha$  at 10 kcps. The movable probe is operated by XYZ motors that enable the performance of spot measurements as well as line and small area scans. The mobile XRF probe moves over the object at a distance of ca. 5 mm and stops for the duration of a single measurement. To ensure the collection of representative data, a line scan connecting some 10 to 40 single measurements was performed at each location. The individual measure-

ments were conducted at 50 kV and 600  $\mu$ A, with an acquisition time of 15 seconds per measurement (live time). Peak fitting and semi-quantitative data evaluation were performed using Bruker's SPEKTRA software.

### **Handling of the papyri**

No special handling is required for reflectography, which can be conveniently conducted through the glass. For XRF measurements, the top glass plate was removed, exposing the corresponding papyrus surface to the X-rays. For each papyrus, we measured the XRF spectra of the underlying glass and papyrus that served as a constant background for the evaluation of the measurements. For each hand, sets of 3–5 line scans (Artax) or single measurements (Elio) were performed.

### **Results**

Table 1 lists the papyri together with the attribution of the hands, the results of the analysis and the techniques used in each case. To improve statistics, in some cases both micro-XRF and XRF analyses were conducted on the same texts. The entry “Carbon” in the column “Ink description” of Table 1 denotes the main type of the ink: no significant change of opacity could be detected by comparing the visible and near-infrared micrographs in any of the texts examined, revealing the presence of carbon in every ink. In addition, chemical elements that were detected by XRF analysis appear in the same column. Here, round brackets indicate uncertainty in the detection, while square brackets point to two cases in which elements were found in the individual texts.

**Table 1 List of papyri and summary of results**

<b>Papyrus</b>	<b>Hand</b>	<b>Ink description**</b>	<b>Methods*</b>
PSI inv. 381 recto	Eudaimon the Elder	Carbon Fe, (K, Ti, Mn, Cu, Zn)	NIRR XRF, micro-XRF
PSI inv. 1402	Eudaimon the Elder	Carbon [S, Fe] <sup>+</sup>	NIRR micro-XRF
PSI inv. 381 verso	Eudaimon the Elder	Carbon	NIRR XRF
P.Flor. III 324 verso	Eudaimon the Elder	Carbon (Fe)	NIRR micro-XRF
PSI inv. 1717 (published as PSI XVII 1681)	Eudaimon the Elder	Carbon	NIRR micro-XRF
PSI inv. 484 (published as P.Bastianini 16)	Eudaimon the Elder	Carbon (Fe)	NIRR XRF
PSI inv. 4335	Eudaimon the Elder	Carbon Ti, Fe	NIRR XRF, micro-XRF
P.Flor. III 386	Col. I: Eudaimon the Elder Coll. II-IV: Unknown I	Carbon	NIRR
P.Flor. III 388	Eudaimon the Elder Col. VIII, 1. 2 Hermias son of Eudaimon the Elder	Carbon	NIRR

\* The primary screening using near-infrared reflectography was conducted in most cases by Francesca Maltomini, Eleni Chronopoulou and Valeria Piano;  $\mu$ -XRF analysis using ARTAX was conducted by Oliver Hahn; XRF analysis using Elio was conducted by Ira Rabin; XRF measurements could not be conducted on P.Flor III 386–388 because of their poor conservation state.

\*\* Round brackets indicate an uncertainty in the detection.

+ The change of the ink probably indicates different writing phases.

++ Metals were found only in the Text B and C.



PSI inv. 1768 (published as PSI XVI 1621)	Col. I: Unknown II Col. II, ll. 1-2: Unknown III Col. II, ll. 3-6: Eudaimon the Elder	Carbon S, K, Fe	NIRR XRF, micro-XRF
PSI inv. 445 recto (published as PSI XVI 1619)	Eudaimon the Younger	Carbon Ti, Fe	NIRR micro-XRF
PSI inv. 323	Eudaimon the Younger	Carbon S, (Ti), Fe, Cu	NIRR micro-XRF
PSI inv. 830	Eudaimon the Younger	Carbon Ti, Fe, Pb	NIRR, micro-XRF
P.Flor. III 387	Eudaimon the Younger	Carbon	NIRR
PL 56 (published as P.Laur II 21)	Unknown I	Carbon (Ti, Fe), Pb	NIRR, micro-XRF
PSI inv. 445 verso (published as PSI XVI 1620)	Unknown IV	Carbon Ti, Fe	NIRR micro-XRF
PSI inv. 1461 (published as PSI XVII 1682)	Text A: Unknown V Text B: Unknown VI Text C: Unknown VI	Carbon [K, Fe] <sup>++</sup>	NIRR micro-XRF
PSI inv. 1646	Unknown VII	Carbon	NIRR XRF

There could be different reasons behind the presence of metal(s) in a carbon ink. Besides the intentional addition of metallic salts into the mixture, metals can enter the ink through the use of metallic inkwells or vessels to prepare and store the ink, or even as a by-product or contaminant contained in the precursor materials, as in the case of glassmakers' soot. Because of this, it is often not clear and rarely possible to prove that small amounts of metals were added deliberately. This is often the case

during on-site measurement campaigns when time restrictions mean that only reflectographic and X-ray fluorescence analysis that offer typological and elemental composition, respectively, can be used. Taking these limitations into account, we must be extremely cautious in attributing the type of ink in cases in which trace amounts of single metallic elements such as iron or copper are detected besides carbon. It is also important to note that attributing iron to the ink on the archaeological papyri is particularly difficult because of the high heterogeneity of iron levels in the papyrus, which is caused not only by the fibrous structure of the material itself, but also by possible contamination during the diagenetic process and by the scattered ink particles resulting from mechanical degradation of ink.<sup>27</sup> The group of papyri presented in this work is no exception, and in the cases of P.Flor. III 324 verso and PSI inv. 484, this poses a challenge when determining whether iron is contained in the ink. Moreover, in the papyrus PSI inv. 381 recto written by Eudaimon the Elder, the background, i.e. papyrus signal of the elements Ti, Mn, Cu and Zn besides that of iron was so high that we repeated the measurements in five locations using two different devices, arriving at the conclusion that only the signal from iron is consistently higher in the inked areas. Use of an imaging micro-XRF device that produces surface elemental maps would resolve the problem, because the distribution of the element contained in the ink would reproduce the text.

In ten cases, however, the amount of metals detected on the inked areas exceeded that in the papyrus to such an extent that we believe that metal-containing components were added deliberately. Let us consider three important examples of the inks discovered in this work.

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<sup>27</sup> Ghigo/Rabin/Buzi 2020.

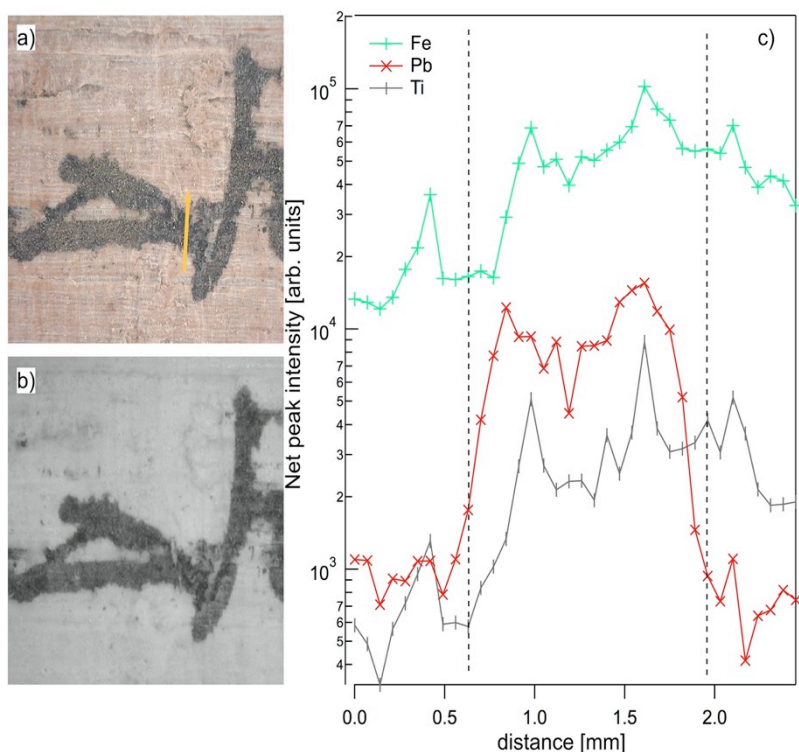


Figure 1. Visible and near-infrared micrographs of the letters “δη”• (a, b, respectively) and XRF intensity profiles of the elements titanium (Ti), iron (Fe) and lead (Pb) along a line crossing the ink (c) on PSI inv. 830. The yellow arrow on the top micrograph (a) indicates the location and the direction of the line scan. Dotted lines on the graph (c) indicate the boundaries of the ink.

Figure 1 shows micrographs of the letters “δη” in visible and NIR light (a, b, respectively) together with the elemental intensity profiles along a line scan crossing the ink on PSI inv. 830. The direction and the position of the line scan are indicated by a yellow arrow on Figure 1b, whereas the dotted lines on Figure 1c show the boundaries of the inked area. Since no change in the opacity of the ink can be observed when comparing the micrographs recorded under visible and NIR illumination, we deduce that elemental carbon must be present in the ink. At the same time, we observe that the intensity of lead (Pb) is an order of magnitude greater in the ink, clearly demonstrating that the ink contains lead. Also, the intensities of titanium and iron with their closely matching profiles are greater in the ink than in

the papyrus. However, the graph shows also that their intensity in the substrate is extremely heterogeneous, with the maximal signal comparable to that of the inked area. Here, however, the peaks and valleys of the abundances of all three elements coming from the areas adjacent to the inks indicate the presence of ink particles scattered around the letters due to mechanical abrasion. The mineral texture of the ink together with loose ink particles outside of the ink and an almost perfect match of the intensity profiles corresponding to titanium and iron suggest the conclusion that the ink contains iron oxide in addition to soot.<sup>28</sup> We can only speculate about the presence of iron oxide in the ink that seems to serve as an extender of soot rather than a natural contamination. The intensity profile of the lead seems to indicate its presence in the ink due to a separate mineral. Though lead has been already found in the soot inks in papyri originating from several different locations, such as Herculaneum and Antinoupolis, the chemical composition of the compound responsible for its presence has never been determined. It was suggested that lead could have been added in the form of a pigment such as galena or minium.<sup>29</sup> In our own mock-up inks, adding galena to the soot inks improved the dispersion of the latter. Furthermore, the authors of a recent analytical study suggested that lead might have been added to the ink as a drying agent.<sup>30</sup> In the present work, ink with the same composition of the additives, albeit in smaller amounts, was found in PL 56 (published as P.Laur II 21). In contrast, inks with titanium and iron as the sole additives were found in another three texts belonging to three different hands, namely Eudaimon the Elder in the PSI inv. 4335, Eudaimon the Younger in PSI inv. 445 recto (published as PSI XVI 1619) and Unknown IV in PSI inv. 445 verso (published as PSI XVI 1620). Since the last two texts appear on both sides of the same fragment, it would be particularly important to verify if they were written with the same ink, even if by two different persons. Unfortunately, the number of measurements conducted on this papyrus is not sufficient to reach an unequivocal conclusion. Also in this case, a bench imaging micro-XRF would be a great help.

Let us now consider the ink from PSI inv. 323, which contains components usually associated with iron-gall inks. Figure 2 shows two micrographs (a, b) with a yellow arrow indicating the location and

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<sup>28</sup> Cornell/Schwertmann 2003:409–412.

<sup>29</sup> Tack et al. 2016.

<sup>30</sup> Christiansen et al. 2020.

direction of an XRF line scan, while the graph on the right shows the intensity profiles of the elements sulphur (S), titanium (Ti), iron (Fe) and copper (Cu) derived from this scan. Here, not only is the signal of all four elements consistently higher in the ink, their intensity profiles also closely resemble each other. As in the previous example, such a similarity of the elemental profiles serves as a proof of the co-presence of these elements in the ink. While the co-presence of iron, copper and sulphur in the ink of PSI inv. 323 can be taken as an indication of the use of vitriol, the presence of titanium attests most probably to the iron oxide component. Therefore, also here we suggest that two components were added independently to the carbon inks, placing this ink in the true category of mixed inks.

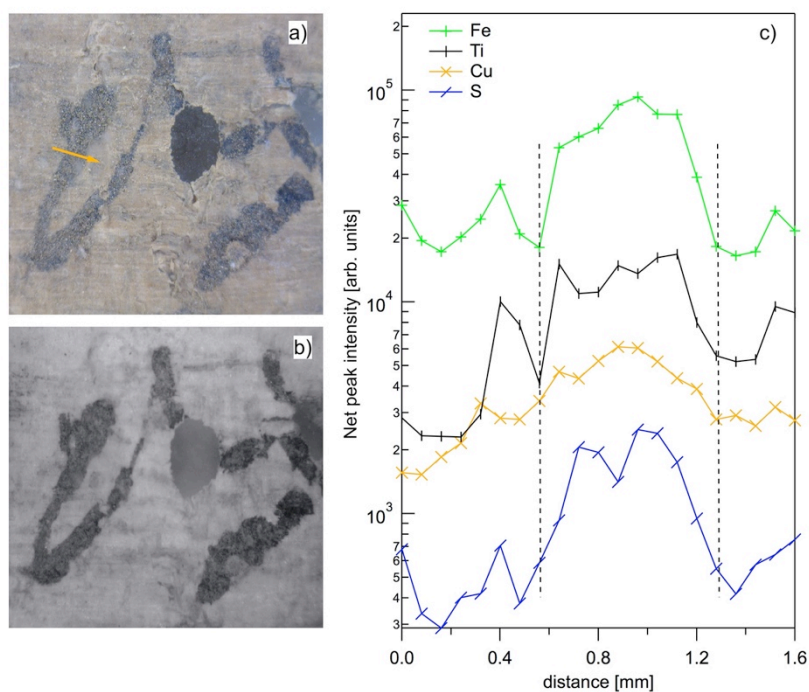


Figure 2. Visible and near-infrared micrographs (a and b, respectively) and XRF intensity profiles (c) of the elements iron (Fe), titanium (Ti), and copper (Cu) and sulphur (S) along a line crossing the ink, as indicated by the yellow arrow on the top micrograph (a) on PSI inv. 323. Dotted lines on the graph (c) indicate the boundaries of the ink.

It is tempting to associate the vitriol in the ink of PSI inv. 323 with one of the earliest pieces of evidence of iron-gall ink, in which green vitriol was used. It is noteworthy that Pliny the Elder mentions *atramentum sutorium*,<sup>31</sup> a substance based on copper (“chalcantho”) but used to blacken leather shoes, ignoring the fact that it was not copper that formed a black complex with tannins, but iron. As mentioned in the introduction, this misunderstanding of the nature of copper and iron sulphates probably circulated in Greco-Roman Egypt, so finding an iron-based vitriol in an ink contemporary with Pliny is more than gratifying.

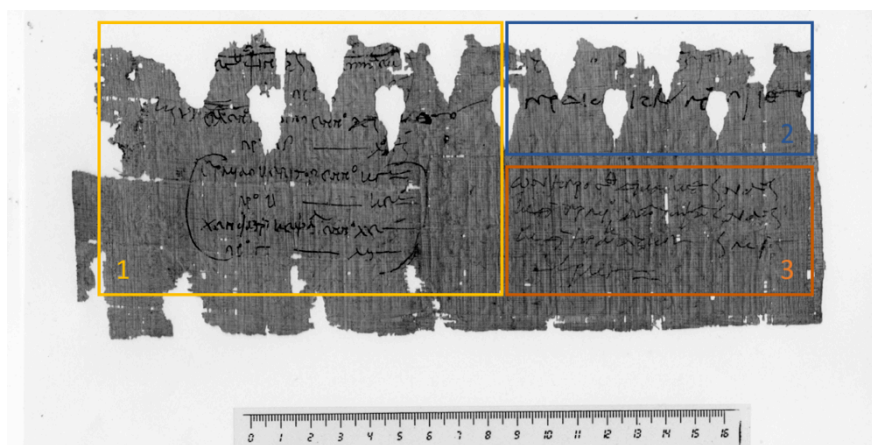


Figure 3. Black and white picture of PSI inv. 1768 (published as PSI XVI 1621). The coloured frames with the numbers inside indicate three different hands.

Figure 4. Visible and near-infrared micrographs (a and b, respectively) and XRF intensity profiles (c) of the elements iron (Fe), potassium (K) and sulphur (S) along a line across the letter “θ” on PSI inv. 1768 (published as PSI XVI 1621). The yellow arrow in the micrograph (a) indicates the approximate length and direction of the scan. Dotted lines on the graph (c) indicate the boundaries of the ink. The intensity corresponding to the element sulphur was multiplied 10 times for the sake of presentation.

<sup>31</sup> Pliny, *Naturalis Historia* XXXIV 32.

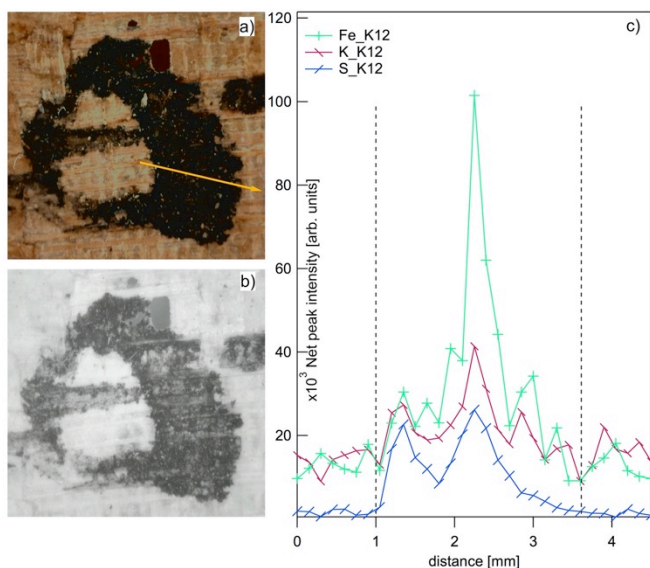


Figure 4

Figure 3 shows three texts that correspond to three different hands in PSI inv. 1768 (published as PSI XVI 1621). Note the diversity of the inks used in close proximity to each other: while hands 2 and 3 used pure carbon ink, an increased abundance of sulphur, potassium and iron was identified in the ink used by hand 1 (figure 4). The matching intensity profiles of sulphur and iron in the graph of the Figure 4c suggests once again that iron vitriol, or maybe iron-gall ink, was added to carbon ink that can be clearly identified by reflectographic analysis in the Figure 4a and b. In this ink, we find no copper, but potassium that we didn't detect in the inks presented before. Potassium may come from different sources. It is contained in gum arabic, a common binder often found in carbon inks. Yet, since potassium is also always present in papyrus, its signal from the ink might be masked by its background signal from the papyrus substrate. Furthermore, alum that can enter the ink as a component of vitriol is another possible source of potassium. Unfortunately, it is impossible to arrive at an unequivocal attribution on the basis of XRF analysis alone. In any case, the presence or absence of small amounts of potassium, copper or zinc in the inks that with great certainty contain iron and sulphur does not necessarily indicate that different vitriols were used as the precursor

salts, since the signal due to minor components in the original admixture might be depleted in mechanically degraded inks.

Summarising, we have found here four different types of inks: a) pure carbon inks; b) inks that contain elevated amounts of lead and iron oxide in addition to carbon and display the mineral texture of a pigment (PSI inv. 830 and PL56 (P.Laur II 21); c) inks of the mixed type containing carbon ink with addition of vitriol/iron-gall ink and iron oxide (PSI inv. 323 and probably by PSI inv. 381 recto); and lastly, d) ink that seems to contain only vitriol in addition to the carbon. We find that all the inks were used indiscriminately in the same household. Note that Eudaimon the Younger used inks of different compositions. We didn't include the inks with Fe/Ti as a separate category because iron oxide-based pigments, for example ochre, seem to be a frequent additive to the carbon inks used here. However, a somewhat larger data set is needed to make a more certain evaluation.

Such a diversity of the inks used within a relatively short period (between the second half of the 1<sup>st</sup> and the beginning of the 2<sup>nd</sup> century CE) and belonging to a family archive would be surprising had we not known from Pliny the Elder that many different carbon inks and methods of extending them existed in the period under scrutiny.<sup>32</sup> Our results raise the question whether people other than professional scribes produced ink themselves. A trade in ink certainly existed in this time, i.e. inks as pigments were goods that could be purchased.<sup>33</sup> So, price becomes an important criterion determining the relationship between the quality of the ink and its composition. The Edict on Maximum Prices issued by Diocletian in 301 CE seems to corroborate this hypothesis, given that the price is stated only for the item “ink” with no further distinction about different types or ingredients.<sup>34</sup>

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<sup>32</sup> Pliny, *Naturalis Historia* XXXV 25.

<sup>33</sup> The word μέλαν appears several times in documentary papyri related to purchases. It sometimes remains doubtful whether it refers to ink properly or to black paint. In some cases, however, the context clarifies the meaning: see for example P.Grenf. II 38 (BC 80), a letter in which the sender asks his father to purchase writing material including ink; P.Mich. II 123 verso col. III.11, 24, 25 (AD 45) and P.Mich II 128 col. II 42 (AD 46), both accounts of the *grapheion* in Tebtunis in which the price paid for μέλαν is mentioned together with that paid for papyrus rolls.

<sup>34</sup> Price Edict of Diocletian XVIII.11a.



Figure 5 compares three different inks: PSI inv. 830 (a, a'), PSI inv. 1402 (b, b') and PSI inv. 1461 (published as PSI XVII 1682) (c, c'). In the first case, the ink has a somewhat powdery and frizzy appearance under visible light but loses much of the mineral texture in the near-infrared image. The appearance corresponds well with the mineral content of the ink. The second ink appears saturated in visible light and dark black and meaty in near-infrared, while the third ink looks rather pale and meagre in both the visible and near-infrared images. In the last ink, the amount of binder might be greater than in the second one. This interpretation is supported by detection of the element potassium, whose increased abundance correlates well with an excess of gum arabic. The fact that different carbon inks were used in the same household clearly indicates purchased, rather than self-prepared ink.

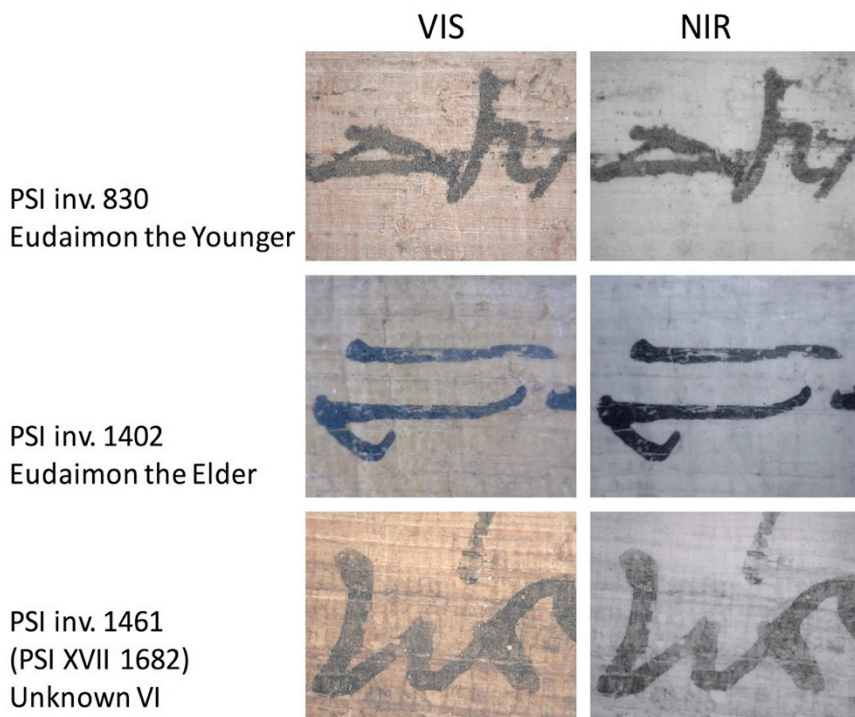


Figure 5. Visible and near-infrared micrographs of inked areas on PSI inv. 830, PSI inv. 1402 and PSI inv. 1461 (published as PSI XVII 1682).

## **Conclusion**

The analysis presented here reports carbon inks ranging from pure to mixed ones with different metallic admixtures that co-existed in Egypt during the 1<sup>st</sup> to 2<sup>nd</sup> century CE. The results obtained on two manuscripts suggest that iron vitriol may already have been used in the manufacture of inks, offering new insight into the materials used in the preparation of black writing media during this period. In addition, the diversity of the inks used in the same household and even by the same person within a short period of time indicates that the inks were purchased rather than self-made and that the exact ink composition was of no interest to a person who would buy his inks rather than make them himself. To estimate the proportion between well-established pure carbon ink and emerging metal-salt-based inks and/or adulterated carbon inks available for purchase, we should continue collecting data on dated and located manuscripts from the time around the beginning of the Common Era.

## **Authors' contributions**

Francesca Maltomini performed near-infrared reflectography on some papyri and wrote the papyrological part of the paper. Tea Ghigo assisted in evaluating the XRF data, interpreting the results and writing the scientific part of the manuscript. Oliver Hahn performed X-ray fluorescence and revised the scientific part of the manuscript. Ira Rabin performed near-infrared reflectography and X-rays fluorescence on some papyri, evaluated the data and wrote the scientific part of the manuscript.

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