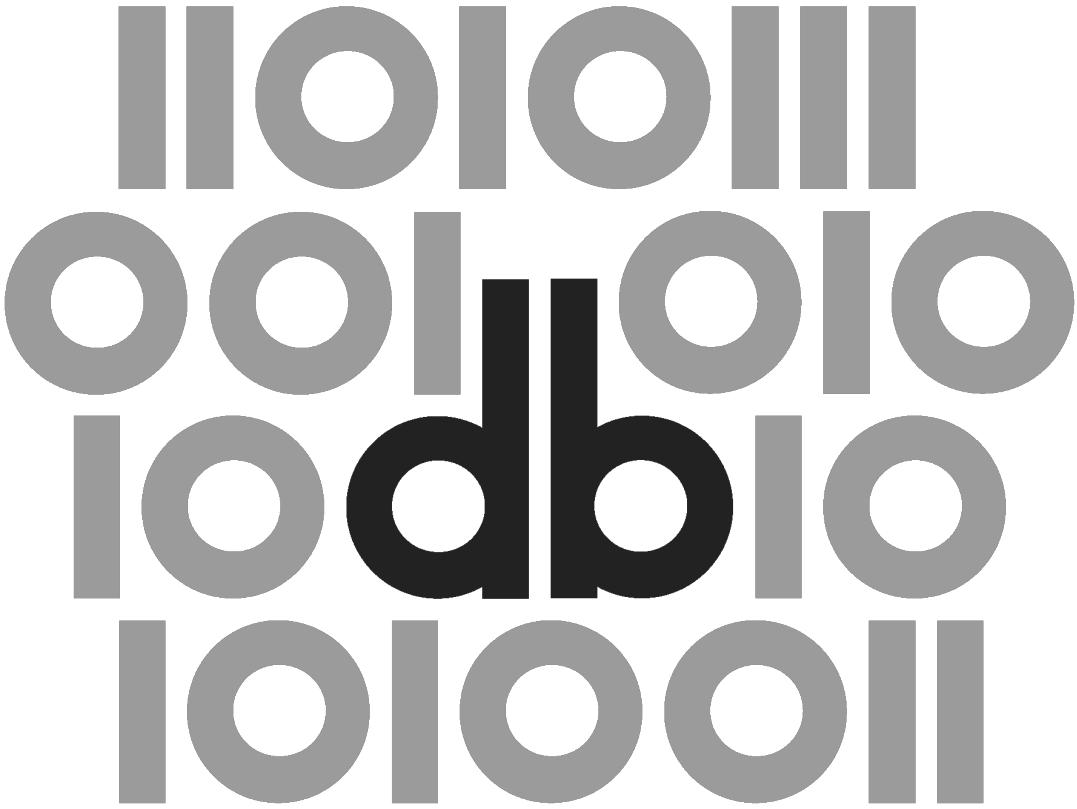

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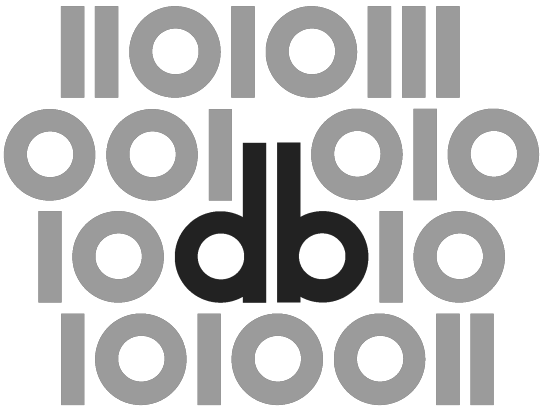


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# Analyzing Inks of the Early Modern Time by Comparing their Features: Assessment of the CodikHum Research Program*

The analysis of inks used in historical documents is sometimes the last resource to answer questions about document authentication or textual origins. It is useful when it comes to matching marginalia to determine the authors of edits in a manuscript or in the margins of a printed book. It is for thesereasons that most research concerning inks has been carried out until now.[1] Until now methods of analysis and measurement relied heavily on spectrometry, on Raman spectroscopy and X-ray fluorescence. Often associated with the study of painters' and illuminators' pigments, the study of inks, however, lacks a broaderperspective, similar to other auxilary sciences in codicology, such as the study of watermarks, paleaography, or papirology. This is the goal of this paper which

* The authors would like to thank Lise Puyo for proofreading the English version of this article.

1 There is no shortage of examples and the few references that follow are in no way intended to be exhaustive: Liliane Bokobza, Jean-Luc Bruneel, and Michel Couzi, "Raman Spectroscopy as a Tool for the Analysis of Carbon-based Materials (Highly Oriented Pyrolitic Graphite, Multilayer Graphene and Multiwall Carbon Nanotubes) and of Some of Their Elastomeric Composites," Vibrational Spectroscopy 74, September (2014): 57–63, https://doi.org/10.1016/j.vibspec.2014.07.009; Jean Bleton, Claude Coupry, and Jean Sansoulet, "Approche d'etude des encres anciennes," Studies in Conservation 41, no. 2 (1996): 95–108, https://doi.org/10.2307/1506520; Stamatis C. Boyatsis, Georgia Velivasaki, and Ekaterini Malea, "A Study of the Deterioration of Aged Parchment Marked with Laboratory Iron Gall Inks Using FTIR-ATR Spectroscopy and Micro Hot Table," Heritage Science 4, no. 13 (2016), https://doi.org/10.1186/s40494-016-0083-4; Oliver Hahn, "Analyses of Iron Gall and Carbon Inks by Means of X-ray Fluorescence Analysis: A Non-Destructive Approach in the Field of Archaeometry and Conservation Science," Restaurator 31, no. 1 (2010): 41–64, https://doi.org/10.1515/rest.2010.003; Oliver Hahn et al., "Characterization of Iron Gall Inks in Historical Manuscripts Using X-Ray Fluorescence Spectrometry," X-Ray Spectrometry 33, no. 4 (2004): 234–239, https://doi.org/10.1002/xrs.677; Oliver Hahn et al., "The Erfurt Hebrew Giant Bible and the Experimental XRF Analysis of Ink and Plummet Composition," Gazette du Livre Médiéval 51, no. 1 (2007): 16–29, http://dx.doi.org/10.3406/galim.2007.1754; Marco Heiles, Ira Rabin, and Oliver Hahn, "Palaeography and X-Ray Fluorescence Spectroscopy: Manuscript Production and Censorship of the Fifteenth Century German Manuscript, State and University Library Hamburg, Cod. germ. 1.," Manuscript cultures 11, (2018): 109–132, https://doi.org/10.17613/M6RX93C96; Ira Rabin et al., "Identification and Classification of Historical Writing Inks in Spectroscopy: A Methodological Overview," Comparative Oriental Manuscript Studies Newsletter 3 (2012): 26–30, https://doi.org/10.25592/uhhfdm.509; Ira Rabin, "Non-Invasive Analytic Tools in Studies of Manuscripts," in Textual History of the Bible, 3D, eds. Marilyn J. Lundberg and Todd R. Hanneken, 114–116 (Brill, 2023). One can also consult the posts published by Patricia Roger in the IRHT hypotheses website: "Étude des encres au carbone, métallo-galliques et mixtes par des méthodes d'analyse non destructive." Post from Les carnets de l'IRHT, 10. September, 2015, https://irht.hypotheses.org/428 and "Étude des encres par analyses spectrométriques." Post from Les carnets de l'IRHT, 10. September 2015, https://irht.hypotheses.org/461.

 DOI: 10.31400/dh-hun.2025.9.8749

is based on the CodikHum ANR project.[2] In a first part, we seek to verify the possibility of sufficiently distinguishing different inks to contrast them, then to cross-reference their characteristics to dertermine their geographical and chronological distribution. The final objective is to begin mapping the inks, which we suspect can be linked to local practices as well as the geological characteristics of the materials used. In a second part, we propose an analytical protocol that respects the rules of conservation of heritage documents by integrating other spectrometric methods into the analytical chain.

## 1. The typology of documents

To demonstrate our methodology, we identified four groups of documents.

| Group/Corpus 1 | Group/Corpus 2 | Group/Corpus 3 | Group/Corpus 4 |
|---|---|---|---|
| ink samples made in the laboratory | Private archives | Archives from the 15th and 16th centuries. Notarial Archives | Literary manuscripts |
| | 8 documents (1525–1680) | Orleans notaries<br>Foix notaries<br>Notaries of Toulouse; Archives of the Parliament. | Corpus of Montaigne's *Essays*<br>Corpus of Pierre Daniel's manuscripts |

**Table 1**. — Typology of the ink datasets examined

The first group was made up of samples with ink pellets manufactured in the laboratory to test the different methods and validate the results.[3] This set allowed us to

[2] Programme CodikHum : ANR-18-CE27-0007. The project summary is visible on the ANR website : `https://anr.fr/Projet-ANR-18-CE27-0007` and on the project website itself : `https://atramentum.univ-tours.fr/`, accessed 30 July, 2025.

[3] The manufacture of inks is based on the following bibliographic data : Zerdoun Bat-Yehouda, Monique. *Les encres noires au Moyen Âge (jusqu'à 1600)*. Paris : CNRS Éditions, 1983. xiv + 437 p. ; Desmarest, L. *Fabrication des encres & cirages : encres à écrire, à copier, de couleurs, métalliques, à dessiner, lithographiques, cirages, vernis et dégras / d'après S. Lehner et R. Brunner*. Paris : Bernard Tignol, Bibliothèque des actualités industrielles, n° 65, 1923. ; our reference inks were made from a basic tannin ink recipe, according to "Ure" including the three basic elements : tanning element filtrate (gall nut), iron sulfate, and binder (gum arabic) for iron- or metal-gallic inks ; carbon black for carbon inks and a combination of the two for mixed inks ; references on parchment (see Delpeyrat, 2002). Reference "metal-gallic" inks manufactured with "historic" alum and vitriol minerals were also made available for these tests. Ballpoint pen inks on paper with more or less strong imprint. Ink alphabet books made with writers or different writing instruments.

overcome the mechanical difficulties resulting from oversized documents. The second set included a set of private archives, purchased on the old paper market at the start of the project. These documents form a coherent whole by geographical origin and date from 1526 to 1680. Some are written on parchment, others on paper.[4] They were used to test every possible analytical method: this was necessary for we were not sure that the methods were in fact non-destructive. Given the constraints of dealing with heritage documents, these methods were eliminated at the end of the study, but we waited to be able to identify the characteristics thus highlighted, even if it meant looking later for other methods to reveal them. The third group, by far the largest, contained documents of known dates and locations. We chose three depositories (Orléans (889 measurement points), Foix (588 measurement points) and Toulouse (a little over 1000 measurement points) and retained additional funds to obtain examples of inks used at different institutions, such as from the Parliament of Toulouse, notarial archives, ecclesiastical funds, parish registers.[5] The last group contains literary texts, themselves grouped in two corpora: the Bordeaux copy of Montaigne's *Essays;* and the preserved books from the library of Pierre Daniel, a jurist from Orléans.[6] From 1588, until his death, Montaigne is preparing the following edition of his book on a printed copy. He then adds thousands of additions and variations in the margins and claims to return numerous times to the text which evolves over time. Additions and variations constitute our corpus. For Pierre Daniel, the marginalia show how this jurist reads and understands ancient texts. The analysis of the marginalia shows the reception of the literature of Antiquity which he often read in manuscripts from the medieval abbey of Fleury.

The last two sets of the corpus warranted different methods of inquiry. In the time allotted, it was impossible to launch an investigation assuming complete coverage of Montaigne's inks due to the very large number of marks of intervention by the author in the margins of the printed book (probably several thousand). In addition, the instruments currently available sometimes do not allow measurements to be taken in the interior margins of books or in areas of waterlogging or duplex overlapping of inks. It was therefore necessary to reduce the corpus and define the points of analysis providing answers to precise philological questions: it was Alain Legros, specialist in Montaigne'manuscripts, who defined the relevant places for the analysis of the inks.

[4] "Des documents martyrs pour étudier les encres anciennes," 4. April, 2024, `https://atramentum.univ-tours.fr/2024/04/04/des-documents-martyrs-pour-etudier-les-encres-anciennes/`.

[5] The list of documents analyzed in these three archive repositories is available on the CodikHum project website.

[6] Pierre Daniel (1530–1603) is an Orléans lawyer. At the time of the wars of religion, he recovered a number of medieval manuscripts from the Fleury monastery in Saint-Benoît sur Loire and also from other monasteries in Val-de-Loire whose libraries were however less important. This collection, then passed to Jacques Bongars, arrived mainly in the funds of the library of the bourgeoisie of Berne. If the manuscripts have been abundantly described, Pierre Daniel's library also included a number of printed works much less often mentioned in the bibliography on this important Renaissance collector.

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## 2. Methodology

Samples documents were used to test the instruments. All documents were analyzed with X-ray fluorescence and spectrophotocolorimeter. Fom the archival documents we identified points of analysis to highlight the variation of inks, i.e. whether they belong to radically different families (inks composed mostly of Fe vs. Zn), or differ by the presence of secondary elements in a lower proportion or by the structure of the ink, visible under the microscope.

The challenge was to find the best possible technique to determine the characteristics of an ink, which would allow us to contrast one ink from another based on what we have called its 'signature'. Since we could not take samples, we worked on exploring different spectrometric tools to characterize inks. We devised means that allowed us to determine the roughness and viscosity of an ink, alongside more traditional means such as colorimetric analysis and determination of metallic and mineral components. In the process we eliminated Raman spectrometry for reasons which we will detail later.

## 3. X-ray fluorescence spectrometry. Microscopy

This is the most widely used method for the analysis of ancient materials, particularly for the identification of pigments since it provides information on the mineral and metallic components of the ink. The data obtained by the X-ray fluorescence spectrometer appear in the form of peaks designating primary elements in the Mendeleev table. Thus, in the Bordeaux copy of Montaigne's *Essays,* on f. 284v, for the analysis point identified under the name e_a_grand *(fig. 1)*, the peaks characterize a predominantly zinc-based ink. The minor components are copper and iron *(fig. 2)*.

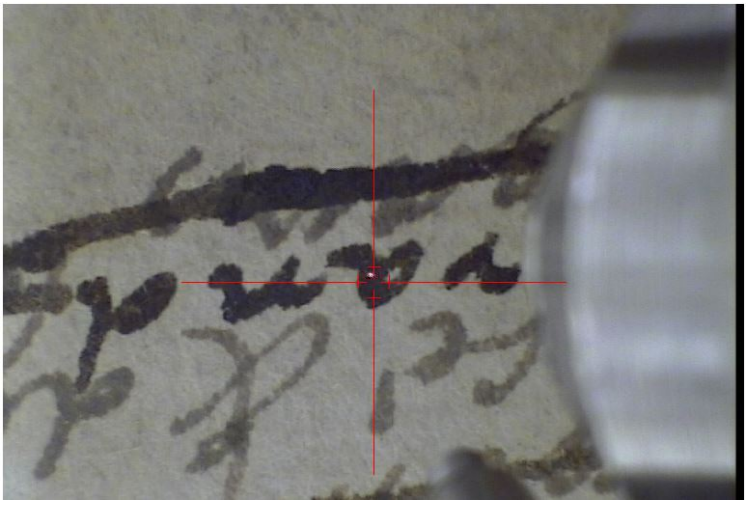

**Fig. 1**. Analysis point on fol.284v – Bordeaux copy of Montaigne's *Essays* – for the X-ray fluorescence spectrometer

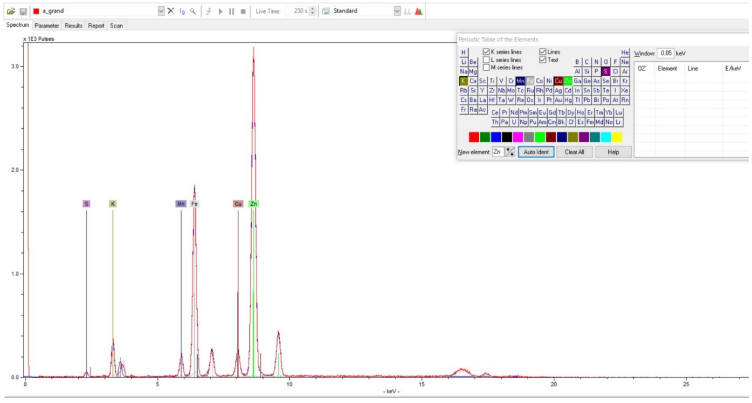

**Fig. 2.** Results of X-ray fluorescence analysis -f.284v, Bordeaux copy of Montaigne's *Essays*

This type of measurement was carried out systematically on all the points of analysis retained in the document. Paper measurements were also taken for all pages considered.

This first method is essential, but it needs to be supplemented by a second series of analyses obtained by the stereomicroscope coupled with a spectrocolorimeter to offer an examination of the colors and the appearance of the ink surface.[7]

These criteria make it possible to classify inks into categories with identical general appearance coupled with identical mineral/metallic composition. For instance, these occurrences of ink with high iron content was found on several leaves of the Bordeaux copy of the *Essays (fig. 3).*

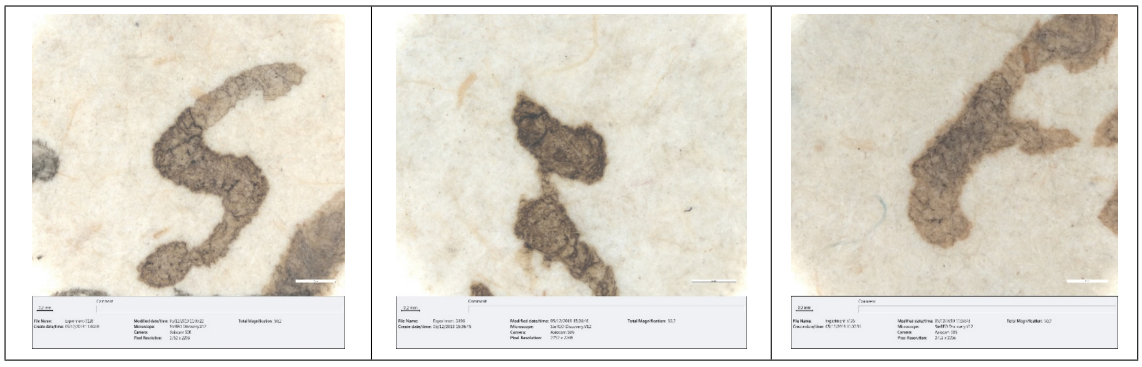

**Fig. 3.** 50x enlargement of ink surface

Comparing observations of the surface and color of the ink also allows for the contrasting of inks in which the same component predominates, but which possibly offers different relationships between the concentration of elements *(fig. 4).*

[7] The equipment used is a ZEISS Discovery Stereomicroscope with motorized column and KL 2500 LCD cold source, equipped with a camera and Y tube for coupling with the SPECTRA VISION optical spectrometer with cooled CCD detector, optical fiber (mono SMA-CZ length 1.8m diam. 0.6mm) and module for stereomicroscope coupling equipped with pinhole and shutter. Diffuse reflection absorption optical fiber spectrometry (ARD-FORS) applies from the extended visible to the near infrared.

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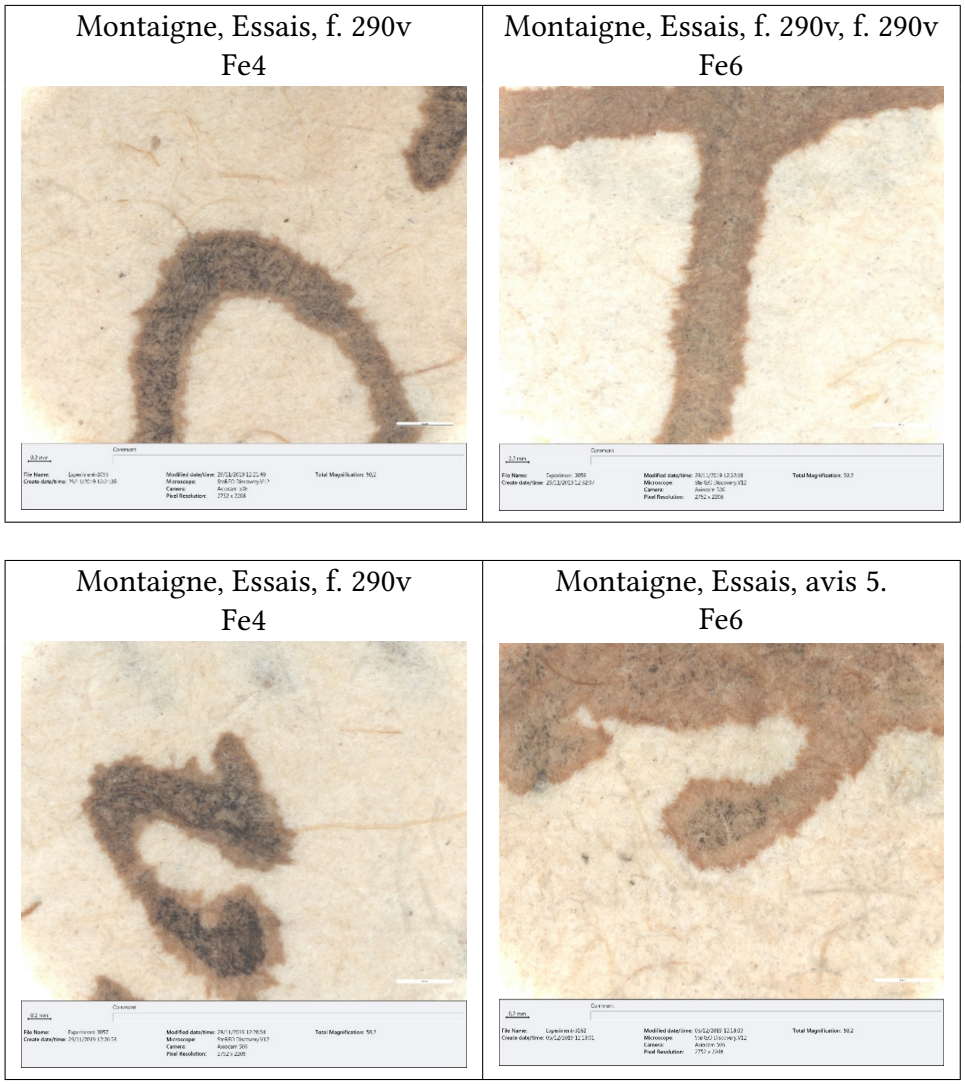



**Fig. 4.** Enlargement of the surface of Montaigne's inks -corpus III-.

## 4. Micro-ATR-FTIR instrumentation

Fourier transform infrared (FTIR) spectrometry makes it possible to highlight emission bands corresponding to molecular compounds. It analyzes the infrared domain *(fig. 9)*.

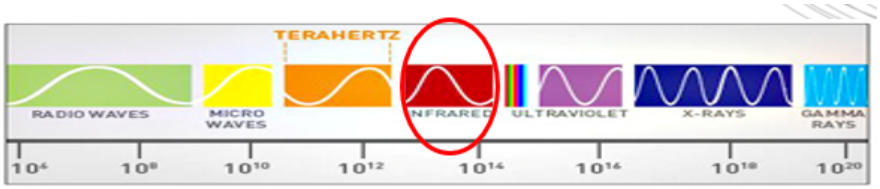



**Fig. 9.** Representative scheme of the electromagnetic spectrum.

We used this method in different modes: ATR,[8] or micro-ATR[9] in reflection mode on corpus II.

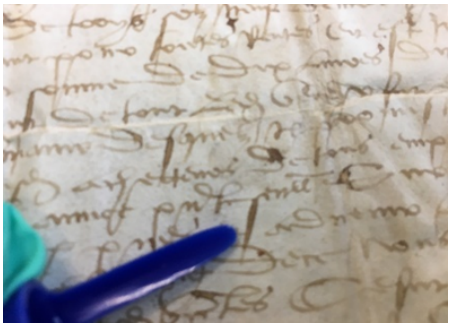
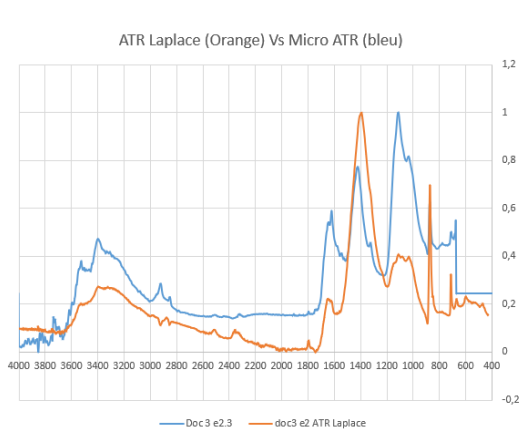
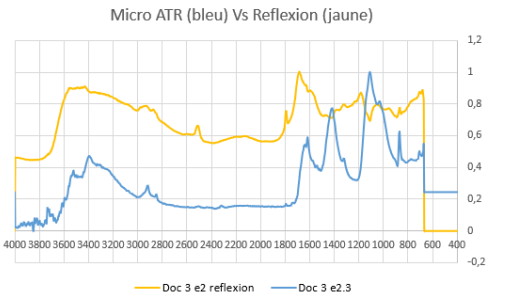


**Fig. 10**. Exemple on doc.n°3.




| ATR Laplace | Micro ATR | |
|---|---|---|
| 3531 | 3528 | OH |
| 3395 | 3393 | OH Water |
| | 2920 | |
| | 2849 | |
| 2521 | | |
| 2349 | | |
| 1792 | | |
| 1645 | 1642 | δOH in water overlapping with vasCOO– in polysaccharide (gum Arabic) / δOH in water |
| 1618 | 1620 | n2 (d) H2O bend |
| 1410 | 1417 | vsCOO– in gum Arabic |
| 1389 | | |
| 1323 | 1323 | d(I-p) C–O–H (phenolic) acide gallique/noix de galle |
| 1140 | 1145 | vC–O gum |
| 1109 | 1115 | |
| 1070 | | |
| 1024 | 1031 | Aromatic asym-, sym- breathing, vC1–C7 + vC–OH (phenol) / vC-O in gum Arabic |
| 872 | 873 | CaCO3 |
| | 772 | Aromatic rings (tannins) torsion (COO ) |
| 710 | 710 | CaCO3 |
| 671 | | |




| Reflexion | Micro ATR | |
|---|---|---|
| 3556 | 3528 | OH |
| 3429 | 3393 | OH Water |
| 2928 | 2920 | |
| 2866 | 2849 | |
| 2507 | | |
| 1686 | 1642 | δOH in water overlapping with vasCOO– in polysaccharide (gum Arabic) / δOH in water |
| 1628 | 1620 | n2 (d) H2O bend |
| 1593 | | |
| 1562 | | |
| | 1417 | vsCOO– in gum Arabic |
| 1381 | 1323 | d(I-p) C–O–H (phenolic) acide gallique/noix de galle |
| 1227 | | |
| 1188 | 1145 | vC–O gum |
| 1130 | 1115 | |
| 1057 | 1031 | Aromatic asym-, sym- breathing, vC1–C7 + vC–OH (phenol) / vC-O in gum Arabic |
| 949 | | |
| 868 | 873 | CaCO3 |
| | 772 | Aromatic rings (tannins) torsion (COO ) |
| 706 | 710 | CaCO3 |

**Fig. 11**. ATR-FTIR and microATR results on doc n°3 -corpus II-.

This technique highlighted *(fig. 11)*, emission bands corresponding to tannin (gall nut) and arabic gum on document no. 3 *(fig. 10)*.

[8] Attenuated Total Reflectance, ATR mode requires contact, the sample is blocked by a "cover press". Measurements made with the Bruker VERTEX 70 spectrometer. The measurement is then made on a part not visible to the experimenter which makes it random. Area analyzed 1mmx3mm duration 30s. Analysis depth 2 to 3 µm.

[9] Other Thermoscientific IN10MX device analysis area up to 20x20µm, analysis duration 30S. The advantage is being able to target the analysis area with a microscope and an integrated camera.

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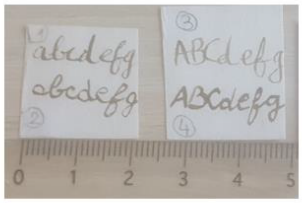
Provided that the analysis area can be visualized, FTIR provides additional information about organic components of the ink without damaging the documents.

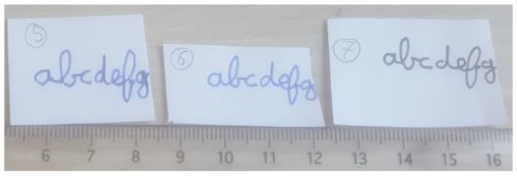
Surface analysis using profilometry has brought us into methods that are little or not implemented in research traditionally focusing on ancient inks. If some of the experiments carried out with a mechanical profilometer did not lead to a directly usable result,[10] the results were much better with the optical profilometer.[11]

## 5. Interferometric microscope

The profilm3D is a compact and easy-to-use interferometric microscope. Measurement by interferometry makes it possible to achieve sub-nanometric vertical resolution, regardless of the magnification/objective/field of view used. However, the measurement quality is strongly dependent on the surface reflectivity of the sample. Strong roughness, local slopes and opacity can influence the quality of the measurement. The measurements focused on corpus I:



| | Scripteur | Outils |
|---|---|---|
| 1 | Scripteur 1 | Outils 1 |
| 2 | Scripteur 2 | Outils 1 |
| 3 | Scripteur 1 | Outils 2 |
| 4 | Scripteur 2 | Outils 2 |



| | Encre | Remarque |
|---|---|---|
| 5 | Encre 1 | Appuie fort |
| 6 | Encre 1 | Appuie moyen |
| 7 | Encre 2 | Appuie moyen |

**Fig. 12.** references inks 1 to 4 -corpus I-.

[10] Tencor P17, allowing 700x300µm mapping in 15 minutes. The analysis area is very limited in size. Flatness of the document is required.

[11] Scientec's 3D profile.

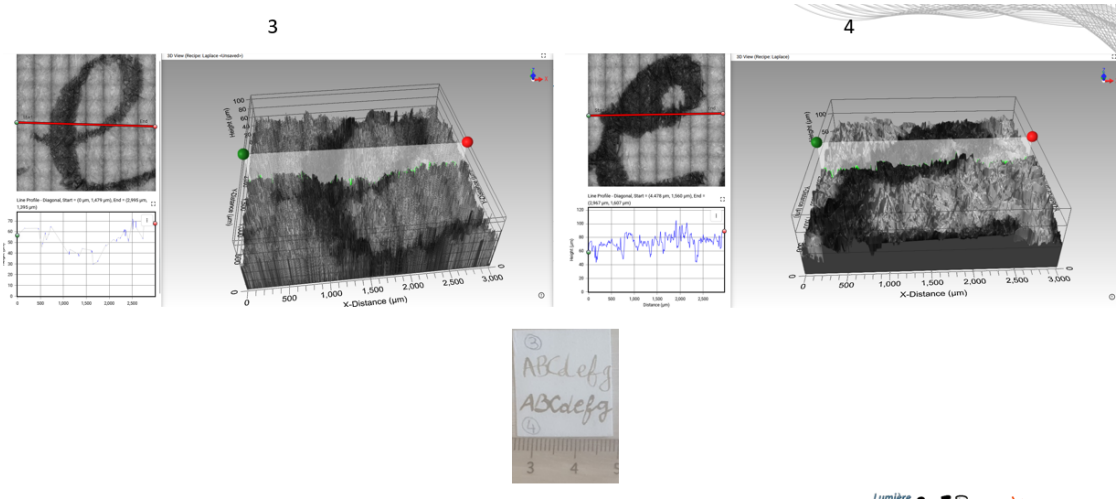



**Fig. 13.** profiles analysis on inks 1 to 4

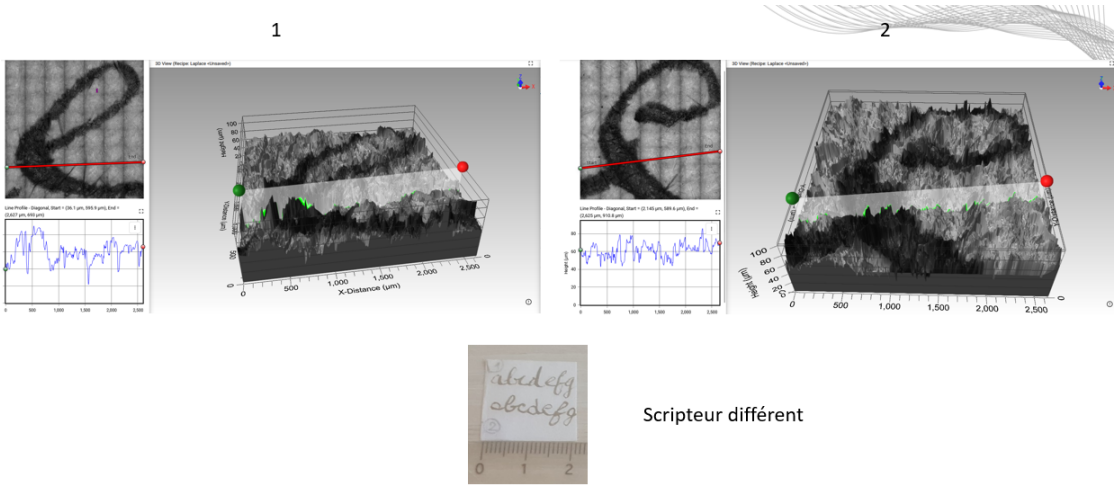



**Fig. 14.** references inks 5 to 7 -corpus I-.

Using this test sample, we can observe that: lines 1 to 4 *(fig. 12):* A Waterman ink -of unknown composition - was used. Ink was applied with a nib on drawing paper of the neutral soft Canson type; two tracings by the same hand and different instruments (goose nib and metal nib) by two hands *(fig. 13).*

Distinctions between the inked area and the surface material are difficult to observe with the height differences

The same surface is used for lines 1 to 4, which is why the roughness have the same order of magnitude and are between 6.4 and 6.9 µm. The pressing of the tool increases the roughness significantly. Furthermore, it seems that each writer influences this roughness *(fig. 13).* Indeed, lines 1 and 3 written by the same writer have a roughness of the same magnitude but greater than lines 2 and 4 (another writer).

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| | Ra ink | Ra substrate |
|---|---|---|
| 1 | 8.128 | 6.435 |
| 2 | 7.483 | 6.899 |
| 3 | 8.480 | 6.399 |
| 4 | 7.332 | 6.545 |
| 5 | 9.217 | 4.338 |
| 6 | 4.884 | 4.259 |
| 7 | 6.188 | 4.127 |

**Table 2.** — Roughness deducted from the profile measurements on inks 1 to 6 -corpus I-.

- Lines 5 to 7 *(fig. 14):*
  The other tracings (5 to 7) were done with a metal and ink pen holder (Waterman ink as well) in different colors on paper. The line is clearly visible and the gap between the inked area and the uninked area is greater than 5 because the user pressed hard. However the gap between 6 and 7 is significant indicating that the user pressed the same way but with a different ink, or the viscosity of the ink plays a role and more or less fills the fibers of the support, or the user did not press in exactly the same way.
  Regarding roughness, the type of writing tool also influences the roughness compared to that of the support, here made of paper (around 4.2 µm).
  In the case where the writer pressed strongly, this roughness is greatly increased (9.2 µm). In cases 6 and 7, the writer tried to press in the same way but with 2 different inks. However, the roughness is very different. Either the writer did not press in the same way or the viscosity of the ink also has an influence on the roughness.

  Test on the printed ink:
- Printed 1959 *(fig. 15),* the difference between the 2 zones is very small.

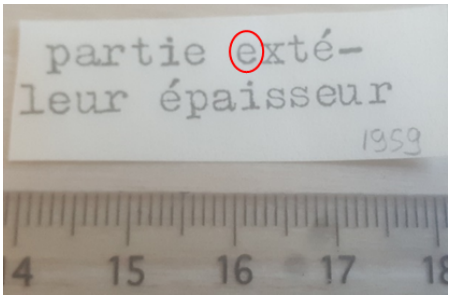



**Fig. 15.** Reference ink -corpus I- printed 1959 document.

After applying multiple filters, height differences in prints are small but measurable *(fig. 16).* They are between 0.065 and 0.072 µm. This difference in height may be linked to the imprint left during printing.

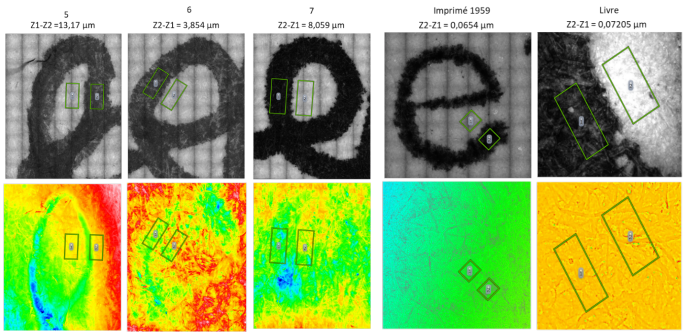
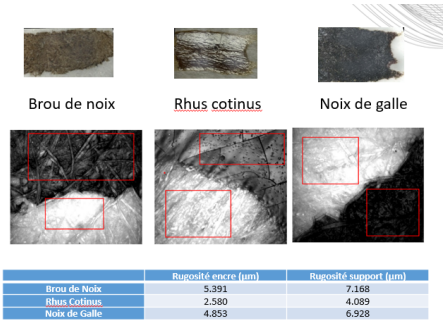



**Fig. 16.** Height différences between surfaces of paper and ink, measured on references -corpus I-.

- + Test of reference tannin-based inks from corpus I:

  References inks composed with different sources of tannins were also analysed. All three inks contain tannin extracted from plants (twigs and wood for Rhus Cotinus / walnut husks / gallnuts), gum arabic, and iron sulfate (to which vermilion has been added for the third ink) *(fig. 17).*




| | Rugosité encre (µm) | Rugosité support (µm) |
|---|---|---|
| Brou de Noix | 5.391 | 7.168 |
| Rhus Cotinus | 2.580 | 4.089 |
| Noix de Galle | 4.853 | 6.928 |

**Fig. 17.** Profilometer results of inks: "walnut husk (left)", " rhus cotinus" (middle) and "gall wallnut" (right)

The support is the same neutral canson paper for rhus cotinus and walnut stain; it is parchment for the third ink.[12] The table shows that the roughness of the ink is lower than of the support as if the ink filled the spaces between the fibers of the support.
In this analysis we observed an opposition between two phenomena:

- The trace left by the tool and the force applied which increases the roughness
- The quantity and viscosity of the ink which fills the fibers of the support and which reduces roughness.

Test on corpus II

It concerns inks from document n°2 and n°5 *(fig. 18, 19):*

[12] They are made using the same basic recipe: tanning agent added with demineralized water, boiling, then a filtrate to which gum arabic is added, followed by iron sulfate.

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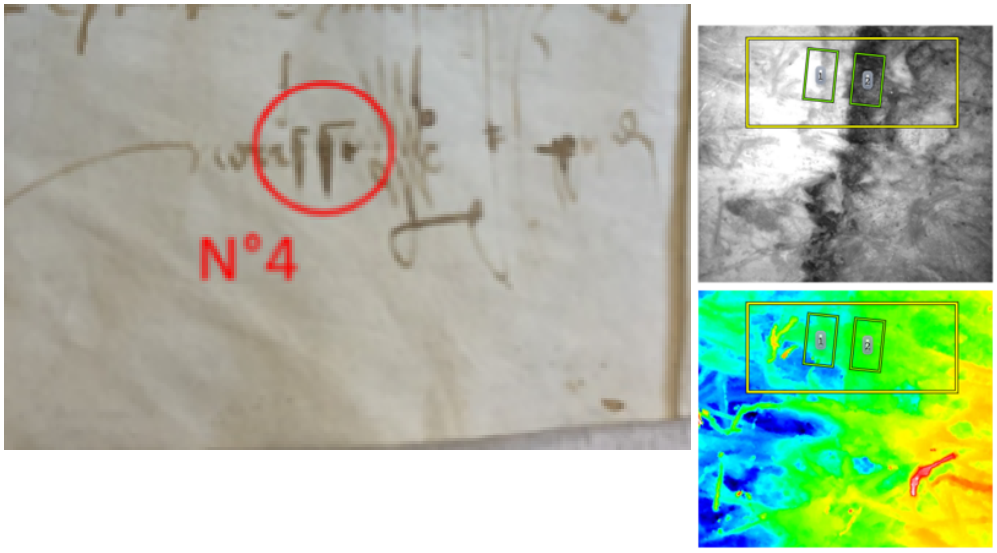



**Fig. 18.** Document 2

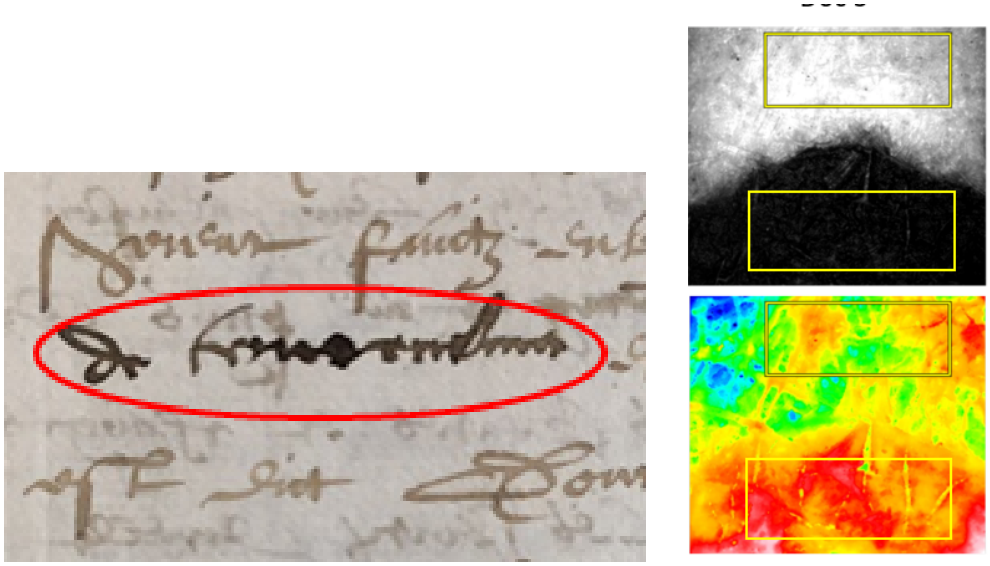


**Fig. 19.** : Document 5

| Doc | Ra support (µm) | Ra encre (µm) | Ra Bord (µm) |
|---|---|---|---|
| 2 | 6,422 | 5,513 | 2,580 |
| 5 | 7,574 | 4,547 | / |

**Fig. 20.** Roughness values of surface material, of ink and of border from document n°2 and n°5 -corpus II-.

The same results are observed on the roughness: that of the ink is weaker than that of the surface material, whether on parchment or paper *(fig. 20)*.

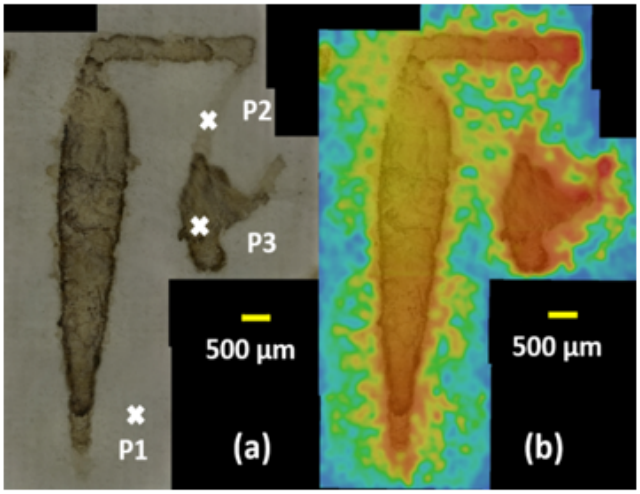
On document 2, the roughness of the support (6,422 µm) is greater than that of the ink (5,513 µm). In addition, an edge effect is observed and in this area the roughness decreases sharply to 2,580 µm, this can be explained by the diffusion of the ink compounds during drying.

For document 5, the inked area (4,547 µm) is less rough than the support (7,574 µm) as for document 2. We can say that in these cases the ink reduces the roughness.

Thus, optical profilometry makes it possible to obtain information on the roughness and surface of inks and supports, in particular the difference in height between an area with and without ink. We managed to determine that the passage of the tool as well as the force applied to write increases the roughness and hollows the fibers. However, the quantity of ink used has the opposite effect, that is to say it reduces the roughness in relation to the support because it fills the space between the fibers. For printed documents, it seems that printing leaves a fairly weak mark and locally reduces roughness.

## 6. Digital Microscope

The digital microscope[13] was tested on corpora I and II *(fig. 21* and *22)*.




Doc 2 signature

**Fig 21**. Digital views from document n°2 ink -corpus II-.

[13] Keyence magnification of 100-1000 or 500-5000; High Dynamic Range mode available; 3D image recomposition possible.

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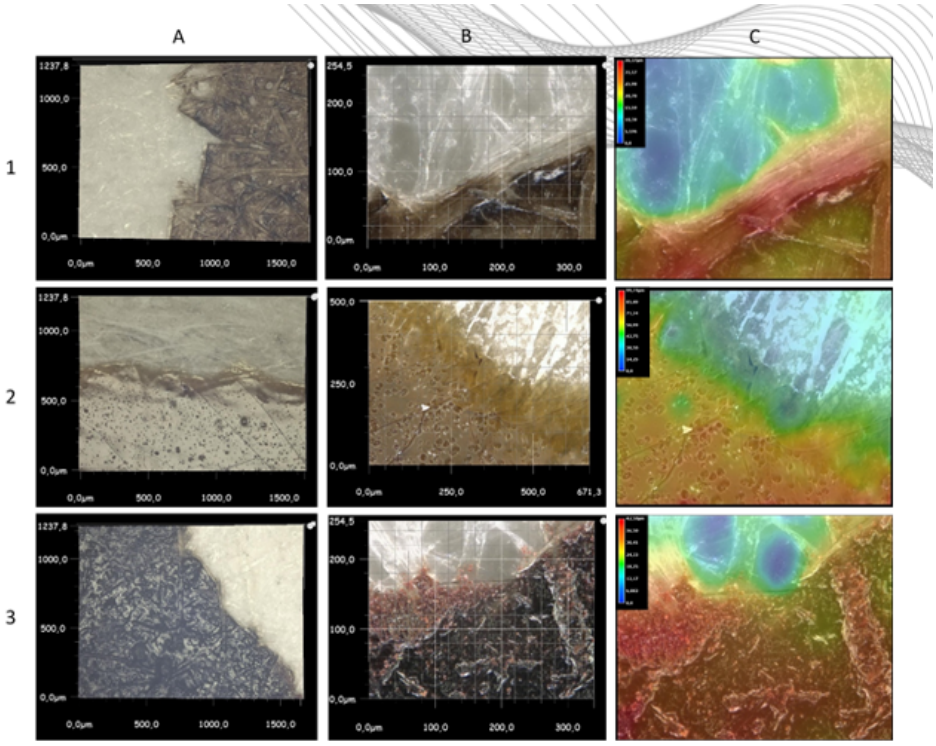


**Fig. 22.** Digital views of references inks composed by different tannins "walnut husk"(left), "rhus cotinus" (middle) and "gall wallnut" (right). -corpus I-.

The analysis is rapid, small-scale observation is facilitated (fiber clearly visible down to µm), the images obtained concerning surface aspects allow relevant comparisons, and the distribution of the ink is highlighted thanks to the color scale.

## 7. Rejected Methods

Alongside these methods which provide essential or new information, other methods tested within the framework of the CodikHum project were ultimately rejected because they were irrelevant or difficult to adapt. Therefore, AFM is not suitable for the analysis of inks, because the roughness of the inks remains too high. The tests were only carried out on manufactured samples or on commercial inks. The operating principle of AFM is based on the measurements of the different interaction forces (ionic repulsion forces, Van–der–Waals forces, electrostatic forces, etc.) between the atoms of the surface to be studied and the atoms constituting the nanometric probe tip, attached to the micro-lever.

The objective of this method within the framework of the project is to characterize the inks at the nanometric scale while remaining representative of the overall behavior.

Topographic measurements (tapping) are only possible on small surfaces (5µmx5µm), which is not necessarily representative of the sample document. In addition, it is difficult to find a measurable area because of the significant roughness of the sample.

Thanks to this method, measurements of mechanical properties (adhesions) are possible (PF-QNM) but in our case the roughness remains too high for this type of measurement. Permittivity measurements (EFM) are only possible when the roughness is low (Ra<10nm) and the thickness is known.

Topographic surface maps highlight that whatever the concentration of iron sulfate, the surface remains quite rough. This observation is confirmed in Figure 23, with a surface roughness (Ra) between 50 nm and 150 nm. In addition, the surface roughness Ra and Rq[14] decreases with the iron sulfate contents. The concentration of iron sulfate promotes the formation of the iron complex and improves the homogeneity of the surface. Finally, the size of the surface studied is small and not representative of the sample. In fact, we test 5-6 zones before finding one measurable.

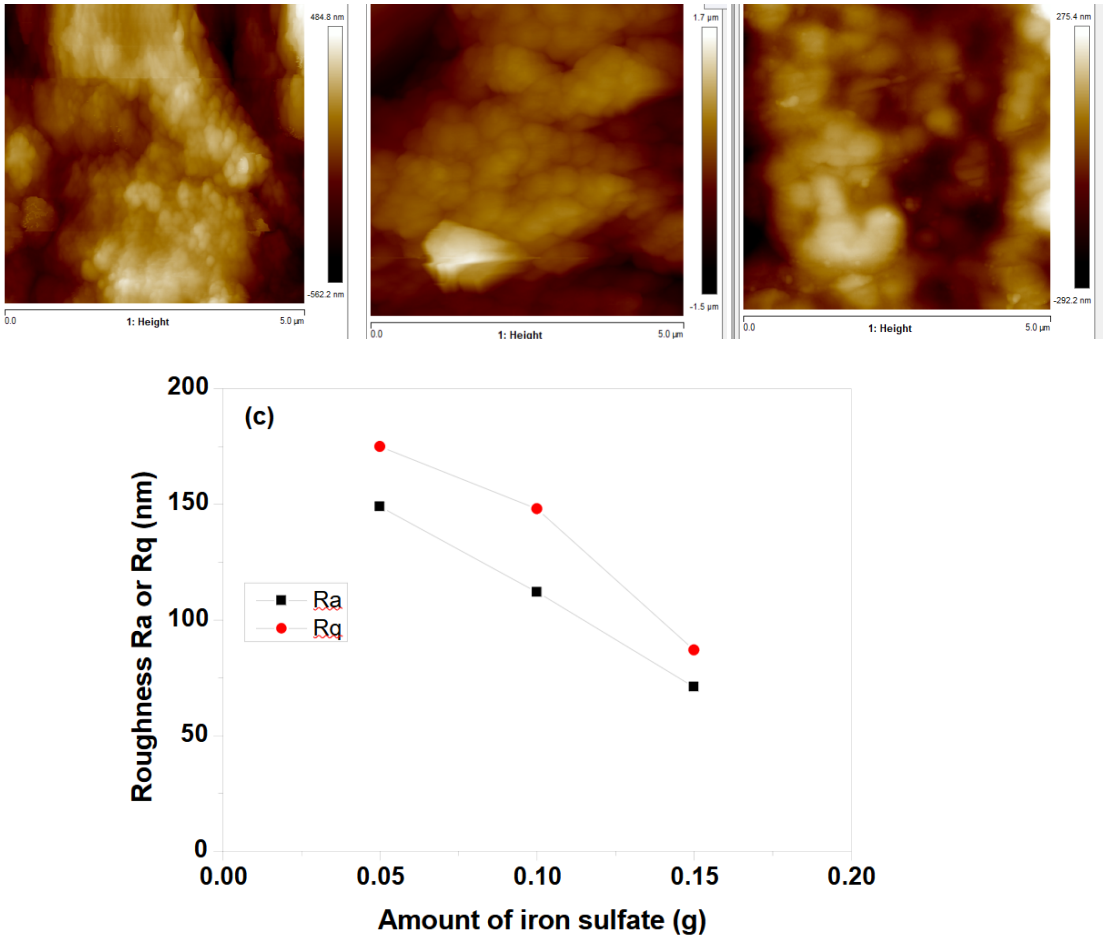


Fig. 23. Roughness depending on the amount of iron sulfate

[14] The parameters characterizing the surface are as follows: - Average roughness (Ra); -Square roughness (rms or Rq).

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For other methods tested, the results obtained are contradicted by the impossibility of adapting the instrument to the reality of historical samples. Thus for the chromameter, a portable spectrophotometer with an integrating sphere and horizontal ergonomics, particularly practical for measuring the color of flat or large samples. It provides simultaneous measurement results in a single measurement sequence: specular reflection included (SCI) and excluded (SCE). With their additional measuring aperture of Ø3 mm, the device adapts perfectly to small samples. The results are presented in the form of L*a*b coordinates, as well as the reflectivity curve as a function of wavelength. The tests were carried out in the laboratory on ink samples: three commercial inks, respectively black, gray and brown and four inks manufactured in the laboratory: a carbon ink, an iron gall ink, a mixed ink based on iron and carbon and an iron and alum based ink. The results make it possible to discriminate between the inks analyzed. Looking at the reflectivity spectrum, the three commercial inks have different behaviors because the colors of these inks are different as shown by the color coordinates.

Regarding laboratory inks, the presence of Alum in the ink seems to have an influence since the reflectivity is lower from 600nm than iron ink, in addition to the difference at 475 nm. This method allows us to obtain colorimetric information quickly. However, the area analyzed is 8 or 3 mm in diameter, i.e. a size significantly larger than that of the letters on the supports of the sacrificial documents, which yields erronous results since the information provided include the ink and the support without it being possible to separate them.

For Gelsight,[15] the interest of the analysis seems more obvious to observe the defects of the support than to characterize the inks. However, it allows the ink to be observed when a very large quantity is deposited on the support.

Tests carried out with different hyperspectral cameras also give contradictory results: if the hyperspectral infrared camera (SWIR) makes it possible to distinguish paper from parchment, it does not allow inks to be analyzed. On the other hand, this analysis is possible thanks to the hyperspectral camera in the visible HSI-VIS. This allows us to determine whether inks are different.

## 8. Raman spectroscopy

Raman spectroscopy is the third commonly used analysis method and for this reason needs a special presentation. The tests were initially carried out using a Labram HR Evolution (LCA)[16] microspectrometer. Other measurements were subsequently carried

[15] The Gelsight is a mobile 3D surface measurement device, a versatile hand-held unit with micrometer accuracy.

[16] ARAMIS xy model 75x50 mm; laser at 785nm to avoid excessive background fluorescence noise induced by the supports, X50 objective, numerical aperture of 0.4, acq time of 60sec. Optical density of 1 and maximum power of 2mW to avoid damage.

out using an Xplora from Horiba Scientific.[17] This system is also equipped with an optical camera for visualizing the object and the focal point of the laser.

The tests were carried out on groups I and II. They made it possible to highlight the emissions due to carbonate (parchment treatment), the iron gall complex and tannins, to the carbon present in the reference inks[18] *(fig. 5).*

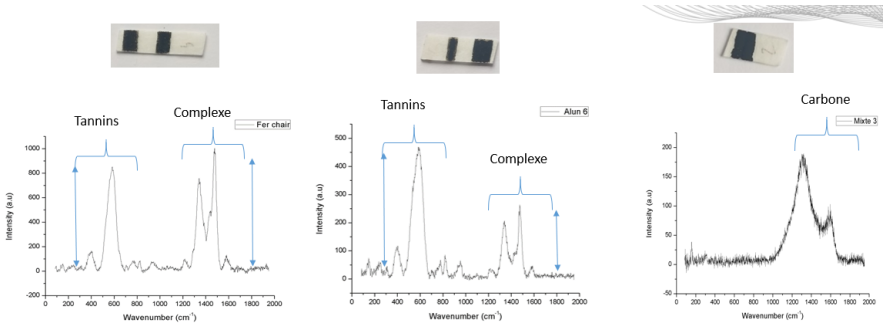


**Fig. 5.** Results from reference's inks -corpus I-.

This technique allows us to distinguish a black carbon ink from a black iron gall ink.

The analyses carried out on the documents from Corpus II show the presence of ferrogallic complex and tannins *(fig. 6, 7* et and *table 3).*

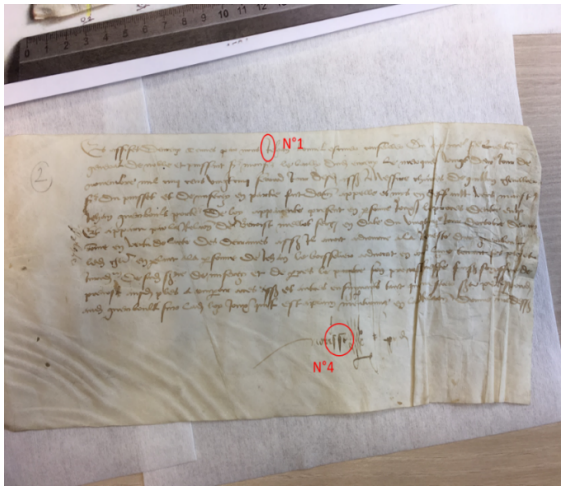


**Fig. 6.** Doc n°2 – corpus II-.

[17] It includes a confocal microscope with X10, X50 and X100 magnification objectives, equipped with a motorized XY Z stage with steps with a resolution of 0.1 micrometer (µm). The confocal microscope is coupled to a high-performance Raman analysis module comprising two diode lasers with excitation wavelengths of 532 and 785 nm, a confocal spatial filtering system allowing a lateral resolution of 1µm x1µm in "Raman" imaging analysis mode (with a 100X objective), a spectrograph with four motorized diffraction gratings and an air-cooled 1024x256 pixel 16-bit Scientific CCD detector. The analysis parameters were as follows λlaser = 785m, 25% filter, grating 1200 lines/mm, slit 100µm, confocal hole 300 µm, objective 50x and acquisition time 2x30 seconds.

[18] The analyzes were carried out by Patrick Mounay from laboratory IMS in Bordeaux, in a first step; then by Benoît Prochet (laboratory Laplace- university of Toulouse) for the CodikHum project. The results that we present here are taken from the report he established at the end of the manipulations and belong entirely to him.

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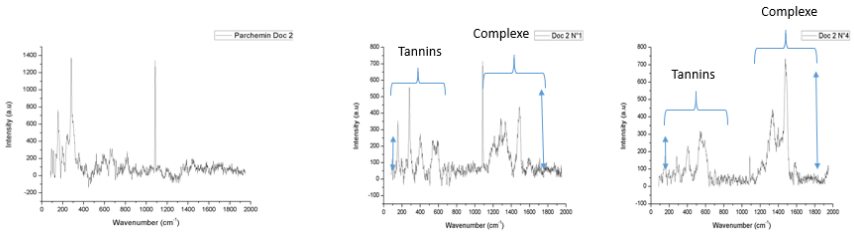


**Fig. 7**. Results from doc n°2 -corpus II-.

| Doc 2 N°1 | | | Doc 2 N°4 | | |
|---|---|---|---|---|---|
| Wavenumber (cm-1) | Intensity (arb. Units) | Normalized value to 1 | Wavenumber (cm-1) | Intensity (arb. Units) | Normalized value to 1 |
| 155 | 354 | 0.50 | 156 | 174 | 0.24 |
| 283 | 556 | 0.78 | 283 | 174 | 0.24 |
| 402 | 277 | 0.39 | 406 | 232 | 0.32 |
| 539 | 232 | 0.32 | 541 | 317 | 0.43 |
| 598 | 228 | 0.32 | 591 | 266 | 0.36 |
| | | | 704 | 101 | 0.14 |
| 1086 | 715 | 1.00 | 1086 | 175 | 0.24 |
| 1214 | 260 | 0.36 | 1222 | 153 | 0.21 |
| 1286 | 368 | 0.51 | 1287 | 267 | 0.36 |
| 1332 | 351 | 0.49 | 1334 | 443 | 0.60 |
| 1389 | 166 | 0.23 | 1398 | 339 | 0.46 |
| 1490 | 441 | 0.62 | 1476 | 734 | 1.00 |
| 1596 | 127 | 0.18 | 1585 | 142 | 0.19 |

**Table 3**. Raman bands on doc. n°2 -corpus II-.

The analyses carried out on document no. 2 show the following results : between point 1 and point 4 *(table 3)*, we have the same bands because they are probably the same ink. There appears to be more ink on point 4, which is confirmed by the higher intensity of the complex bands.

Despite the brown color of the ink, the presence of certain bands confirms the presence of a metallogallic complex *(fig. 7)*. X-ray fluorescence analysis shows that the metallic compounds in this ink are iron, zinc and copper. The color can also be explained by the degradation and aging of the ink.

If we compare with the reference inks, the complex bands are similar. On the other hand, the tannin bands are different because the source of tannins may be different.

Other characteristics concern documents on paper. In the spectra of inks on these documents, the characteristic bands of the ferrogallic complex and tannins are present, as in the spectra of inks on parchment ; however, other bands appear in the 750-950 cm-1 region, which may be related to the paper.

Regarding the relative intensities between the complex bands and the tannin bands, they are similar for documents 5 and 8. On the other hand, they differ depending on the points analysed on documents 6 and 7.

The X-ray fluorescence data from document 5 highlight the same proportion of elements between the 4 measurement points, which could explain why the Raman spectra from document 5 are similar *(table 4 and fig. 8).* However, on point 1, the presence of bands between 1800 and 2000 cm-1 has not been attributed; they may be due to the presence of organic compounds not present in the reference inks.

For document 8, the X-ray fluorescence and Raman data are similar between the different points measured.

In these two examples, the results between X-ray fluorescence and Raman can be correlated within the same document, but it is more complicated to compare between documents. Indeed, the Raman spectra of documents 5 and 8 have many similarities but the proportion of elements present is clearly different since Zinc is in the majority while it is almost not present in document 8.

Regarding document 6, the fluorescence shows a similar composition with a difference of 5% only on Zinc.

Regarding document 7, the inks are mainly composed of iron but they are different with the other elements. The differences observed could be linked to other phenomena.

The coupling between these 2 methods could make it possible to distinguish inks within the same document.

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| Doc 5 pt 1 | | | Doc 5 pt 2 | | |
|---|---|---|---|---|---|
| Wavenumber (cm-1) | Intensity (arb.Units) | Normalized to 1 | Wavenumber (cm-1) | Intensity (arb.Units) | Normalized to 1 |
| 158 | 137 | 0.12 | 156 | 213 | 0.10 |
| | | | 249 | 244 | 0.11 |
| 401 | 410 | 0.37 | 403 | 466 | 0.21 |
| 561 | 876 | 0.79 | | | |
| 589 | 657 | 0.59 | 593 | 1289 | 0.59 |
| 651 | 269 | 0.24 | 653 | 516 | 0.24 |
| 705 | 199 | 0.18 | 705 | 248 | 0.11 |
| 786 | 90 | 0.08 | 775 | 238 | 0.11 |
| 829 | 79 | 0.07 | 819 | 267 | 0.12 |
| 932 | 158 | 0.14 | | | |
| | | | 1094 | 376 | 0.17 |
| 1175 | 116 | 0.10 | 1120 | 261 | 0.12 |
| 1210 | 159 | 0.14 | 1222 | 303 | 0.14 |
| 1287 | 352 | 0.32 | 1287 | 878 | 0.40 |
| 1339 | 484 | 0.44 | 1334 | 1386 | 0.63 |
| 1393 | 446 | 0.40 | 1393 | 978 | 0.45 |
| 1482 | 1105 | 1.00 | 1472 | 2192 | 1.00 |
| | | | 1586 | 236 | 0.11 |
| 1656 | 141 | 0.13 | | | |
| 1698 | 132 | 0.12 | | | |
| 1749 | 167 | 0.15 | | | |
| 1828 | 218 | 0.20 | | | |
| 1876 | 338 | 0.31 | | | |
| 1925 | 458 | 0.41 | | | |

| Doc 5 pt 4 | | | Doc 5 pt 6 | | |
|---|---|---|---|---|---|
| Wavenumber (cm-1) | Intensity (arb.Units) | Normalized to 1 | Wavenumber (cm-1) | Intensity (arb.Units) | Normalized to 1 |
| 159 | 172 | 0.12 | 243 | 185 | 0.27 |
| 195 | 173 | 0.12 | | | |
| 248 | 198 | 0.14 | 298 | 142 | 0.21 |
| 300 | 234 | 0.17 | | | |
| 407 | 384 | 0.27 | 401 | 303 | 0.44 |
| | | | 550 | 489 | 0.72 |
| 591 | 1079 | 0.77 | 594 | 419 | 0.62 |
| 646 | 530 | 0.38 | 654 | 114 | 0.17 |
| | | | 707 | 134 | 0.20 |
| 773 | 292 | 0.21 | | | |
| 823 | 268 | 0.19 | | | |
| 975 | 209 | 0.15 | 939 | 122 | 0.18 |
| 1103 | 157 | 0.11 | | | |
| 1222 | 268 | 0.19 | 1212 | 168 | 0.25 |
| | | | 1287 | 272 | 0.40 |
| 1322 | 997 | 0.71 | 1343 | 464 | 0.68 |
| 1393 | 606 | 0.43 | 1397 | 286 | 0.42 |
| | | | 1431 | 221 | 0.32 |
| 1474 | 1405 | 1.00 | 1487 | 681 | 1.00 |
| | | | 1592 | 121 | 0.18 |

**Table 4**. Raman Bands of inks Doc n°5

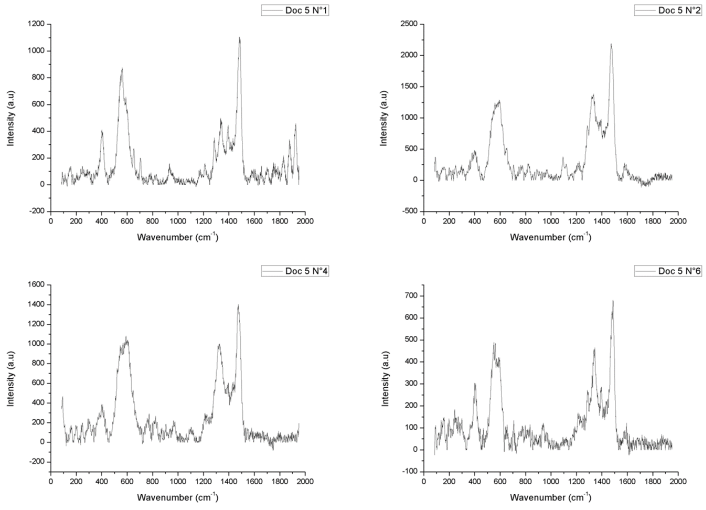


**Fig. 8**. Raman spectra of Inks Doc n°5

We would obtain answers of the same quality with an FTIR analysis, without the disadvantages that Raman analysis presents for particularly fragile heritage documents.

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Raman is a technique used to highlight the presence of the iron gall complex thanks to the presence of characteristic bands. By comparing the relative intensities it is possible to indicate the more or less significant presence of the complex in relation to the tannins and vice versa.

In some cases, the presence of fluorescence background noise or a very noisy signal can prevent the interpretation of the spectra. In addition, the low thickness of the ink and its interaction with the support can explain the presence of ink and support bands on the spectra, making the interpretation more complex. Other effects are not taken into account when the reference ink spectra are compared with the corpus, such as the effects of aging and degradation.

In addition, Raman analysis uses a laser focused on the document and if the power of this laser is not controlled it could locally degrade the sample. This makes, in our opinion, this method of analysis incompatible with the constraints of the conservation of heritage documents and, for this reason and despite the information it provides, we will not retain it in our protocol.

Finally, we tested a dozen ink analysis methods that resulted in a comprehensive protocol, and which could lead up to new instrumentation. This protocol is now established : it combines proven methods, new ones, and a method still being tested at the time of this report which relies acoustic waves – the latter being very primissing.

To our knowledge, the use of such protocol, the implementation of acoustic waves, or the analysis of the surface and roughness of the ink have never been implemented in the analysis of historical documents.[19] It remains to be seen whether the protocol will move from experimentation in the laboratory to implementation in the library, taking into account the modifications needed to existing instruments - not to mention the constitution of a comprehensive instrument which remains to be invented.

## 9. Partial results

The second pillar of our research program concerns the creation of a common framework. It would indeed be of no use to have good analytical instruments if we cannot reliably compare results, particularly on the central question of the provenance of documents. We therefore launched the creation of a repository funded by departmental repositories in Orléans, Foix and Toulouse. The aim is to find repositories which offer sufficient availability of archives from the 15th and 16th centuries and, if possible, a wide variety in the institutions producing the documentation (group 3). To this dated and localized documentation, we have added a literary corpus (group 4). It is from this second set that we borrow the following results and procedures, established from the marginalia added by Montaigne in counterpoint to the 1580 edition of the *Essays*, on his own copy of the text. The points of expert analysis were defined by Alain Legros, a well-known specialist in Montaigne and his manuscripts who is also the author of the philological conclusions that can be drawn from these analyses.

[19] The tests were carried out by Professor Gilles Despaux of the Institute of Electronics and Systems (UMR 5214 – University of Montpellier). We hope to be able to develop these tests in a future version of the CodikHum project.

On literary corpora or on the corpus of archival documents, X-ray fluorescence analyses and those using spectrophotocolorimetry were implemented. The protocol is identical, whatever the document. The analyses successively give the metallic and mineral composition of the ink, two x8 and x50 magnifications which allow a clear vision of the surface of the ink (presence of borders, more or less dense black grains, color compared a universal color table). This set is safe and sufficient to discriminate the inks, even though the implementation of other techniques would offer numerous other information on the inks studied.

The conclusions relating to this corpus, established by Alain Legros, can be found on the CodikHum project website.[20] The approximately fifty sheets on which the analyzes relate reveal a lot of different inks. The distribution of inks on the same page offers an illustration of the "jumping and frolicking" look claimed by Montaigne. We borrow from this review article this information which summarizes in broad strokes what the precise analysis of inks can bring to the understanding of the genesis of Montaigne's text.

The great diversity of inks in Fe_maj and Zn_maj (more than ten inks in all, as a reminder) shows that during the last four years of his life, Montaigne constantly brought back to the construction site the hybrid text of EB, whether during dedicated campaigns, yet to be determined, or through meetings, during leafing through or partial re-readings. It seems that the author-corrector first used Fe_maj inks (first spelling corrections and very first additions) and only later switched to Zn_maj inks, which is evidenced in its own way by the title -frontispiece where, after crossing out horizontally and obliquely in Fe_maj the printed lines which presented the expanded edition of 1588 as the "fifth", he added in Zn_maj that it was indeed a "sixth edition", consecrated by a Virgilian epigraph which essentially says that the child's book has grown like a rumor that cannot be stopped… EB then became a working example (was he the only one?), open to "infinite trials". We see Montaigne "at work", at least during his last four years of life, rectifying, deleting, modifying and above all considerably lengthening his text, as he seems to have already done for previous editions, proceeding by accumulation of successive notes more or less assorted, a bit like old parchment rotuli which were extended if necessary, with a new piece roughly sewn to the previous one.

Without going further into the detail of the results obtained on Montaigne's *Essays* (this will be the subject of another publication), the analysis of the inks highlights both the interest of these analyses and the limits of the experience.

On the side of interest, there is, obviously, that of providing information on the genesis of the text, including in cases where we do not have information coming from a stylistic or paleographic analysis. Clearly, in these cases, ink discrimination moves the debate forward decisively. Before systematizing the ink analyzes within the framework of the CodikHum program, other tests carried out on the ex-libris of books that belonged to Rabelais[21] or on the books of Montaigne marked with a b in the

[20] `https://atramentum.univ-tours.fr/2023/06/26/les-encres-de-montaigne-sur-lexemplaire-de-bordeaux/`.

[21] These tests were carried out as part of the Rablissime program directed by Marie-Luce Demonet and funded by the Centre-Val de Loire region.

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upper right corner had shown that the analysis of the bookplates also made it possible on the one hand to contribute to the authentication of the works by matching inks and on the other hand to install elements of chronology in the reconstruction of the history of the collection.

Two other issues remain to be resolved before moving on to a systematic investigation. The first is the improvement of a more precise ink discrimination and data processing. The database we designed batch imports the data from the instruments.[22] This was sufficient for this test, but it can be improved to facilitate more sophisticated data analyses.

## 10. Conclusion and perspectives

While this digital tool is essential, it still needs to be improved to fully fulfill its role. In addition to phisico-chemical analyses of ink, we need to better understand the ingredients used to produce ink to campare them with what we see in our investigations. The ink recipes known so far, those published by Monique Zerdoun or those found in Canepari's book, give the architecture of the recipe and the ingredients. In many cases, this is not enough to explain the traces of other elements entering into the composition of the ink. These traces, if we are to believe Canepari,[23] and before him Agricola, could be attributed to the furnaces in which the mixtures were prepared, but we can just as easily find the explanation in the impurities coming from the ores themselves. It is therefore appropriate to return to the texts with a slightly different point of view, closer to that implemented by the historians of metallurgy. It would also be appropriate, in the near future, to cross-reference the ink data with the information in account books, grant registers, or any document likely to shed light on the origins and form of the ingredients used in the production of the ink. The aim would then be to understand whether links could be established between the nature of the metals imported and the results of analyses carried out on heritage documents. We could, for example, ascertain whether the traces revealed are due to impurities in the materials used, depending on where they were extracted, or whether we need to look for explanations in the instruments used to process the metals.[24] For the Renaissance, we can add printed documents to the classic tax documents, such as the "tariffs", which determined the rights of passage for goods in transit, and private accounts, whether for printing works or the houses of great personalities. Although we are not certain

[22] The database can be consulted at `http://atramentum-bdd.org`, accessed 30 July, 2025.

[23] Pietro Maria Canepari, *De atramentis*, Venice, 1619. The text was republished twice in 1660 and 1718. It is cited quite critically by Montfaucon in the *Antiquitates graecae et romanae*, who however notices a jumble of useless things in the volume. Canepari's text is above all compilatory in that it takes up both ancient sources (Pliny) and the observations of earlier Renaissance scholars including Agricola and Cardan. Montfaucon is perhaps a little harsh : the chapters on pyrites and those on writing inks deserve better than this judgment.

[24] For example, Olivier Thuaudet has carried out a detailed study of the copper trade, which is frequently used in the composition of inks Olivier Thuaudet, "Approvisionnement et circulation du cuivre et de ses éléments d'alliage en Provence du XIIIe au XVIe siècles," in *Les métaux précieux en Méditerranée médiévale*, édité par Nicolas Minvielle Larousse et al., 301–318 (Presses universitaires de Provence, 2019), `https://doi-org.proxy.scd.univ-tours.fr/10.4000/books.pup.40420`.

that we will find references to inks in private archives, which are not very frequent, we do know that they exist in those of the Plantin printing company in Antwerp, for example.[25]

With regard to the digital representation of early modern inks, the Atramentum database now allows the storage and comparison of ink recipes. In time, we will integrate data from bibliological treatises published during the Renaissance, both in Latin and in the vernacular, into. The integration of these data, unstructured or structured according to a schema different from that of the recipes, will imply a revision of the organisation of the database itself. To achieve a more global explanation of Renaissance inks, which we believe is possible, much remains to be done. The increase in the volume of data from the analyses, their alignment with their historical provenance and the creation of an integrated measurement instrument are the three axes of future research to create a tool for understanding the history of inks.

[25] Mentions of ink purchases appear in several registers of the printing press archives. For example in register 722 which brings together invoices and orders for paper, ink and vermilion; in register 750, we find the accounts relating to bookbinders and illuminators for a period covering the years 1560–1669. The ink maker, for these years, is called Joris Berger and he is known as a worker of the company in another document. In register 756, we learn that the main supplier of ink to the Plantin house is called Van Esche. The register also attests to a typology of inks which distinguishes between weak inks (accounting documents of June 15) and hard inks (accounting documents of July 20 and 26). Colin Bloy in a 1972 study points out other ink makers active in Parisian printing circles: for example Guillaume de Launay, active in Paris in 1522, Noël Guyton who fulfilled the same office in Reims or Jehan Odet in Lyon. See Colin H. Bloy, *A History of Printing Ink, Balls and Rollers*, 1440–1850 (London: Wynkyn de Worde Society, 1972).

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