

Supplementary Material: Iron-gall inks molecular data and recipes

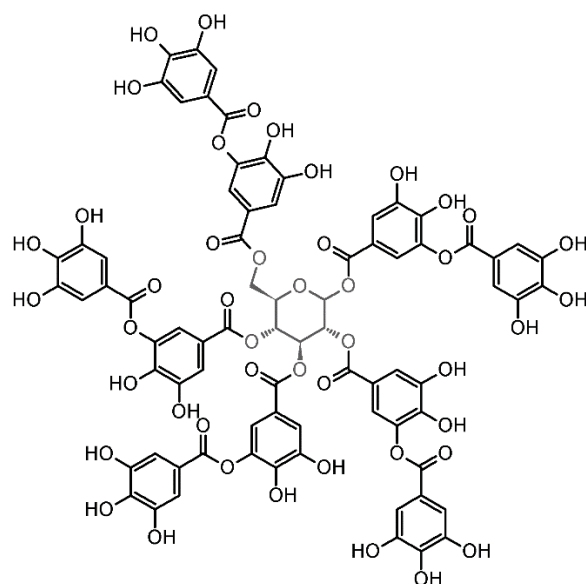


Figure S.1: Molecular structure for tannic acid as described by suppliers.

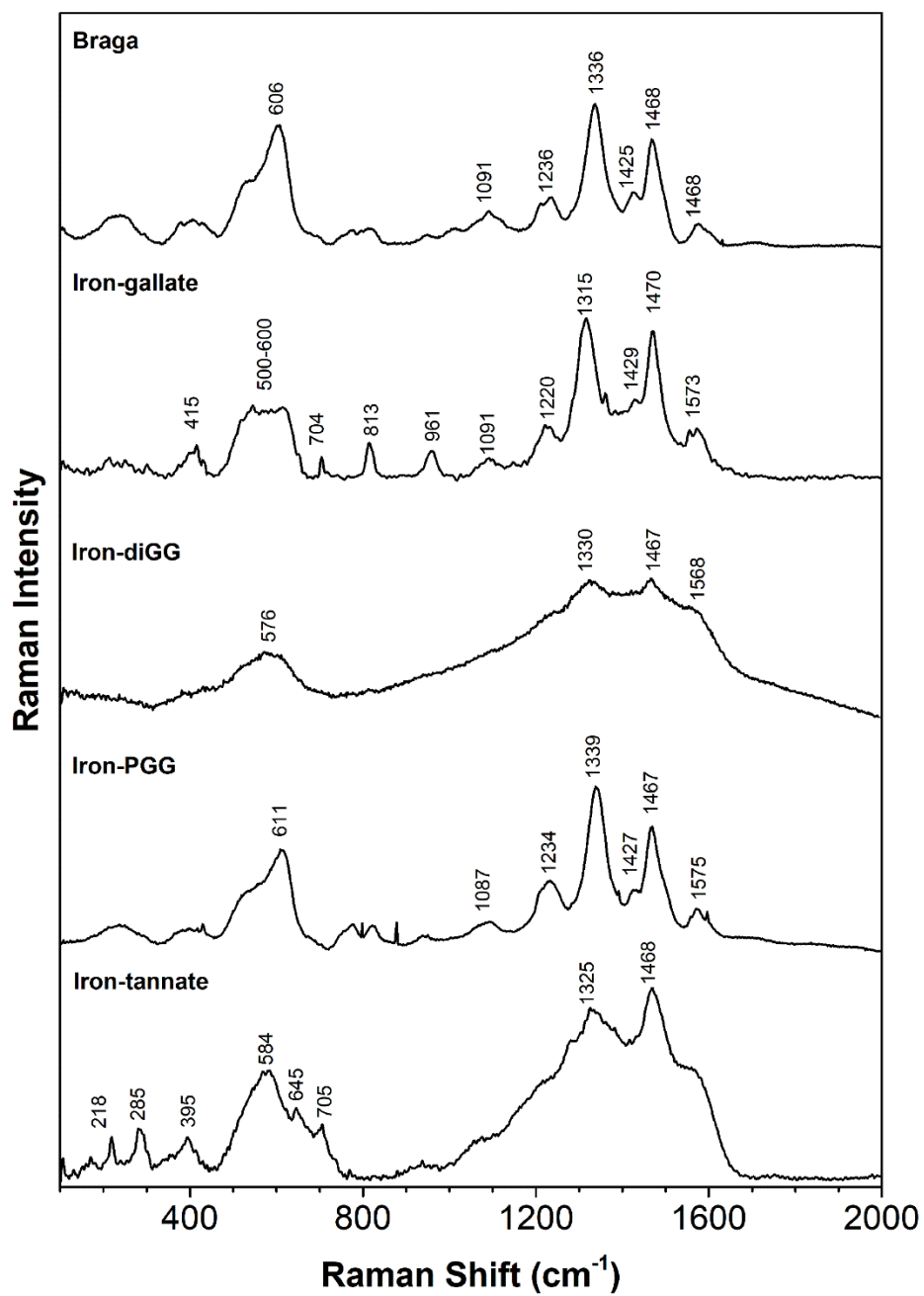


Figure S.2: Raman spectrum for the *Braga* ink, applied on filter paper compared with spectra for the iron gallate, di-galloate, penta-galloate and tannate precipitates, $\lambda=785\text{nm}$.

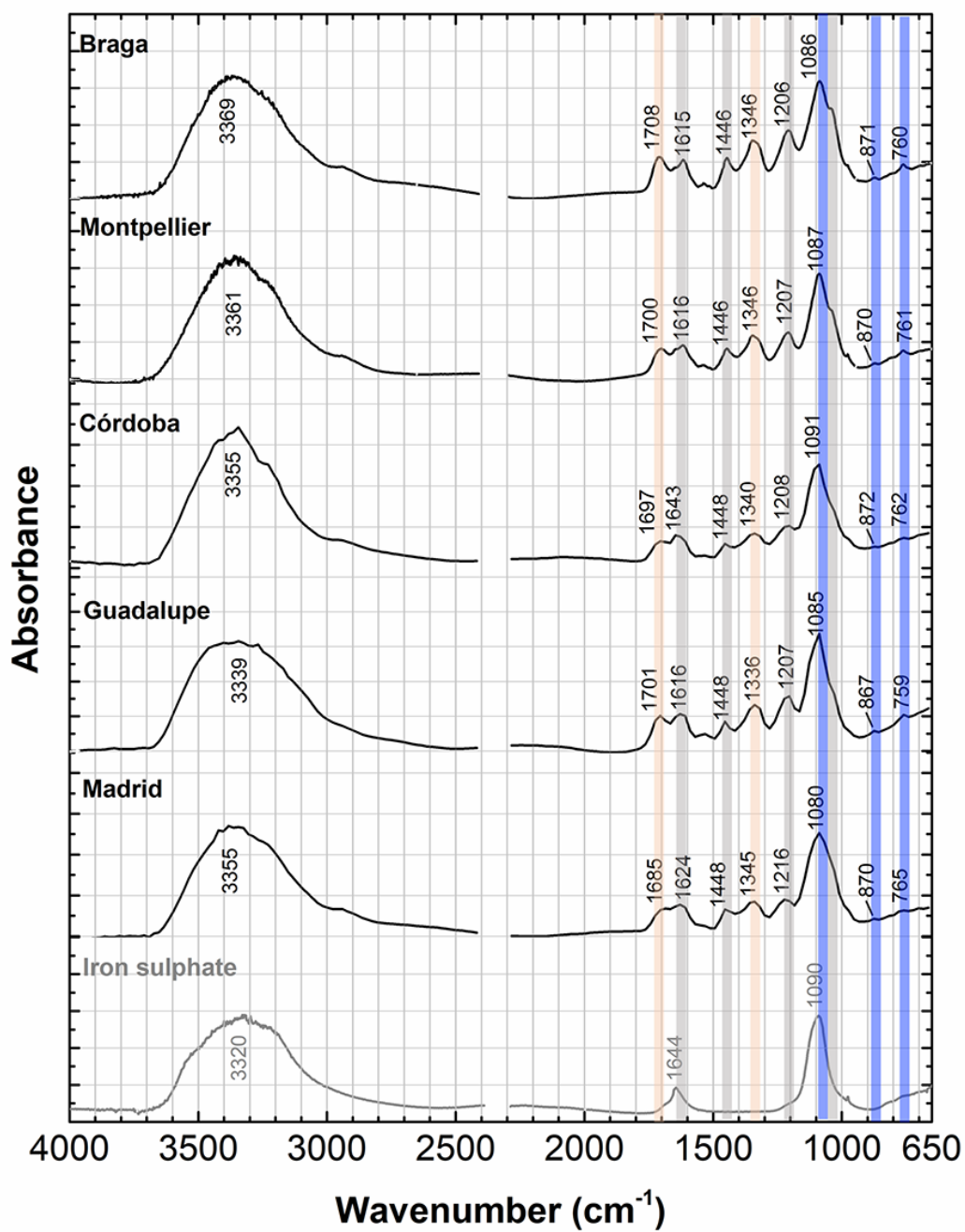


Figure S.3: Infrared spectra for the Iberian inks, and iron sulphate reference for comparison. Assignments for iron gall inks are based on Falcão and Araújo 2013 [36]: grey shading, characteristic common bands for "tannins"; red shading, vibrations presented by hydrolysable tannins; blue shading, distinctive bands, marker bands for gallotannins

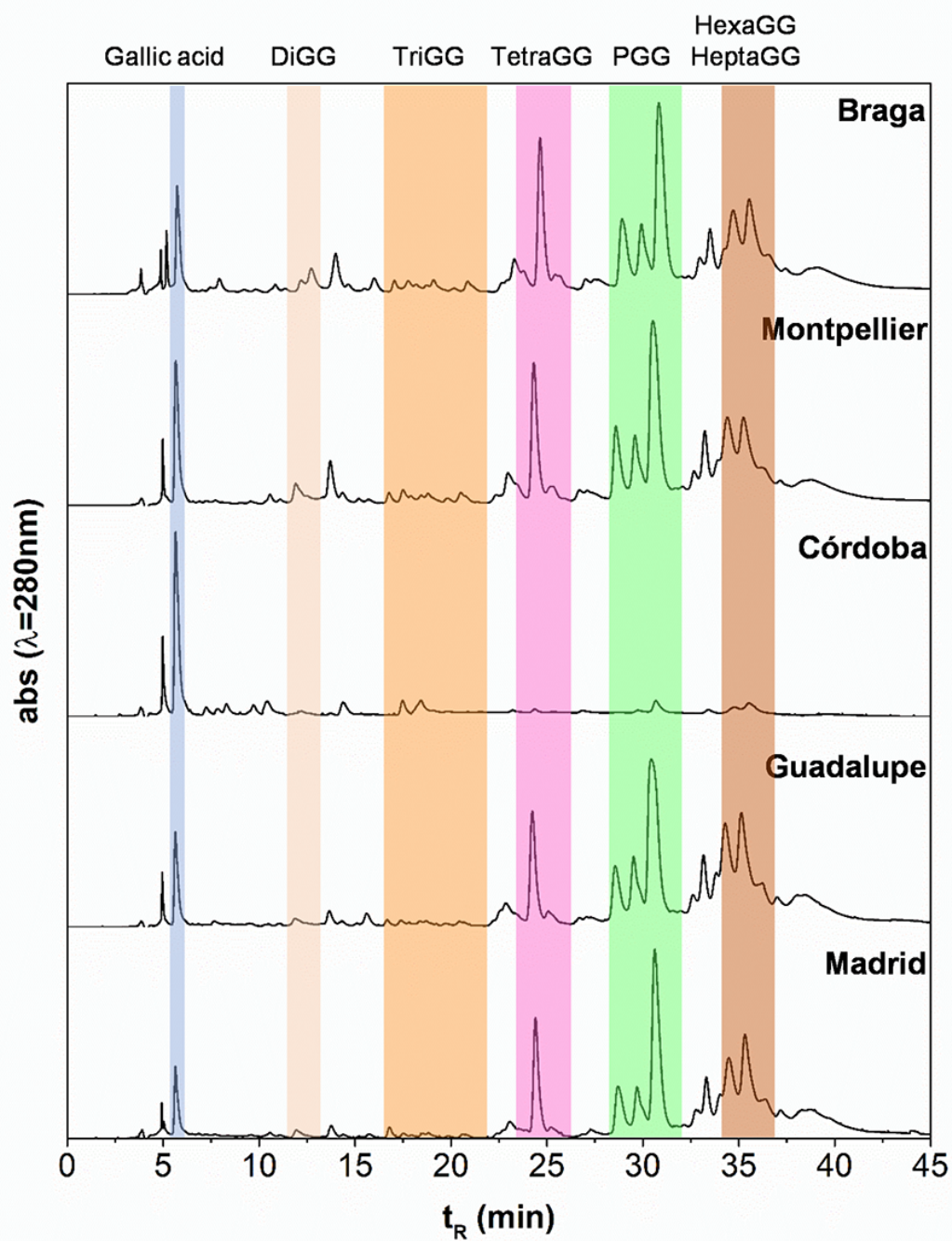


Figure S.4: HPLC–ESI–MS chromatograms of all the extracts from the Iberian recipes. Gallic acid elutes at *ca.* $t_R = 5$ min.

Table S.1a – Main steps and ingredients used to prepare iron-gall inks from the Iberian treatises (transcribed below).

						
	Water	Other	Galls	FeSO ₄	Gum arabic	Extraction
Braga	33mL	16.6mL vinegar	3.12g	12.5g FeSO ₄	1.56g	Boil immediately until volume is reduced to 2/3.
Montpellier	50mL	-	1.43g	0.95g FeSO ₄	0.95g	<u>3 days, RT</u> After it is heated and reduced to 1/4. Filtered
Córdoba	50mL	-	1.91g 0.95g pomegranate	1.91g FeSO ₄	0.95g	<u>8 days, RT</u> After it is slowly heated until boiling point. Filtered
Guadalupe	37.5mL	12.5mL white wine	5.6g	3.75g FeSO ₄ 1.87g CuSO ₄	1.87g	<u>6 days, RT</u> After it is heated with low temperature for 10 minutes Filtered
Madrid	-	40mL white wine	2.21g	2.21g FeSO ₄ 0.18g Al ³⁺	2.21g	<u>9 days, RT</u> Filtered

Table S.1b – Transcription of the selected Iberian writing ink recipes.

Arcebispaço de Braga, cx.31:

“Recepta de tinta Toma de gallhas I onça e quebranta as meudas e lança as a ferver em hua libra d'auga terçada de vinagre branco e fervam tanto que mingue as II partes e lança lhe meia onça de goma e toma de azeche IIII° onças muudo e peneirado e lança lho dentro e mexe com hum paaço e folge assy hua noite e hum dia e será muito booa” [22].

3.12g of galls were ground and added to 33mL of millipore water and 16.6mL of white vinegar and boiled, until it is reduced to two parts of the volume. After 1.56g of gum arabic were added, under stirring until it is completely dissolved, after which 12.5g of previously sifted FeSO₄ were added to the solution. The solution was stirred with a branch from a fig tree and left to settle one night and one day.

Montpellier fol.233v:

“Para tinta. Toma una libra de acije y 1 libra y media de agallas y 1 libra de goma. Rompe las agallas y ponlas en remojo en tres cuartillos de agua durante 3 días. Después cuece y reduce casi 3 partes de agua y si hierva cuélala. Una vez colada mete dentro una onza de goma y revuelve hasta que se ponga líquida toda la goma. Después en dicha agua fría mete 1 onza del dicho acije y remueve y déjalo estar así durante un día. Después cuélala y métela en ampollas, etcetera” [24].

1.43g of galls were crushed and added to 50mL of millipore water and left to extract at room temperature for 3 days. After this time, the solution was heated and reduced to $\frac{1}{4}$ and then filtered. 0.95g of ground arabic gum were added, under stirring until dissolution, and, after cooling, 0.95g of FeSO_4 were added. It was left to settle for one day and then filtered.

Protocolos Córdoba fol.58v:

“Para faser tinta buena toma vna olla de vn asunbre e echalde tres quartillos de agua e echalde dos onças de agallas bien quebradas e contía de vna honça de cáscaras de granadas agras sy las oviere o sy non sean de granadas duses e estén en remojo contía de ocho días. E después coseldas sobre fuego de carbón muy manso quanto escomiençe a feruir e non más, e después dexaldas esfriar e desque fuere bien fría sacáredes las agallas coladas e espremidas e echaldas fuera. E tomad dos honças de buen asiche e moleldo e echaldo en vna haltanna e cobrildo en agua e esté fasta que sea desfecho e echaldo en el agua de las agallas e meçello muy bien e dexaldo asentar vn día, e después colalda con vna vedija de lana que cayga en otra olla. E en lo colado echáredes vna honça de buena goma e dende a dos días será fecha” [20].

1.918g of well crushed galls and 0.959g of pomegranate peel were added to 50mL of millipore water and left to extract for 8 days at room temperature. After this period, the solution was slowly heated until boiling point and after cooling it was filtrated. 1.91g of FeSO_4 were placed in a glass cup and covered in water and dissolved, and this solution was later added to the extraction. The solution was left to settle for one day and then filtrated. After, gum arabic was added and left to settle for two days.

Libro de los Oficios de Guadalupe fol.201r-v:

“Para un açumbre de tinta son menester seys honças de agallas e quatro honças de201 v// azige, e dos ho[nças de goma, e dos de caparroso.] As de saber que echamos t[anta agua como tin]ta queremos sacar, salvo que anidimos [a un a]cumbre de agua un quartillo de vino [blanco] puro, bueno para el cozer, e por esta man[era] podéis acresçentar o amenguar. E a[se de] fazer en esta manera, echada el agua e vino en una olla limpia, todo junto, has de echar en una escudilla las agallas bien partidas, e en otra el azige, e en otra la goma, e del agua que está en la olla con el vino, echa sobre el azige fasta que se cubra, e en la goma eso mismo cada uno aparte, e en el agua que quedare, echa las agallas. E así lo has de tener çinco o seis días, meçiéndolo muchas vezes con un palo de higuera cada uno por sí. Después desto, echa las agallas con su agua en una olla e ponlas sobre el fuego, el qual a de ser manso, e cuézelas tanto fasta que le pueda dezir dos vezes el salmo de miserere mey, e has de ser avisado que no se salga por çima al ferner. E después tira la olla del fuego e déxala un poquito, e échala en otra olla202 r// [colándola, e luego, antes de que se en]fríe, échale [dentro la goma e méçela] bien porque desha[ga, e después] de otro poco, antes que se acabe de [enf]riar, échale el azije, mirando que no echas [la tierra,] más que se quede en el suelo de la escudilla, [e después] que todo esté bien frío, has de tener la capa[rros]a molyda e échasela dentro, e dende a [un] rato tórnoalo a colar, e échalo en las vasijas en que ha de estar” [23].

5.6g of crushed galls, 3.75g of FeSO_4 and 1.87g of gum arabic were placed in three separate glass cups. 37.5mL of millipore water and white wine (12.5mL of wine) were distributed by the cups in the following manner: enough solution to cover the FeSO_4 and the gum arabic and the rest for the galls. The solutions were left to settle for 6 days, stirring every day with a dried branch from a fig tree. After this time, the galls solution was heated with low temperature for 10 minutes (60°C) and filtered. After a while, and without letting it be too cold, the FeSO_4 and gum arabic solutions were added, always under stirring. After being at room temperature, 1.87g of CuSO_4 were added and the solution was filtrated.

Ms 9226 de Madrid, fol.192r-v:

“Para haber un açumbre de tinta echa açumbre y medio de vino blanco doncel 6 onzas de agallas quebrantada[s] y dexalas estar 9 días meneándolas mucho. [Luego] al cabo de ellos cuela este vino en otra olla y echa en el 6 onças de caparrosa y otras 6 de goma. Luego echa Açucar piedra y piedra alumbre y añir de cada [¿esta?] media onça y tenla al sol dos o tres días mene[an]dolo bien, o a fuego manso. Y quando este echa guardala en vaso limpio en lugar fresco” [26].

2.21g of crushed galls were added to 40mL of white wine and left for 9 days, at room temperature. After this time, the solution was filtered. 2.21g of FeSO₄ and 2.21g of gum arabic were added to the solution, as well as 0.18g of brown sugar, 0.18g of indigo and 0.18g of alumen, and the solution was slightly heated at 60°C.

Table S.2 – Unit conversion used for the medieval reconstructions [34-35].

	Volume		Mass	
	Azumbre ¹	Cuartillo	Pounds ²	Ounces
Lisboa	-	-	446.4 g	28.68 g
Salamanca	2 L	0.5 L	460 g	28.75 g
Córdoba	8 L	2 L	460 g	28.75 g
Cáceres	5.2 L	1.3 L	456 g	28.5 g
Madrid	8 L	2 L	460 g	28.75 g

1) 1 azumbre = 4 cuartillos;

2) 1 pound = 16 ounces.