

Supplementary Material: New Insights into Synthetic Copper Greens: The Search for Specific Signatures by Raman and Infrared Spectroscopy for their Characterization in Medieval Artworks



Figure S1 Representative pigments for each group.

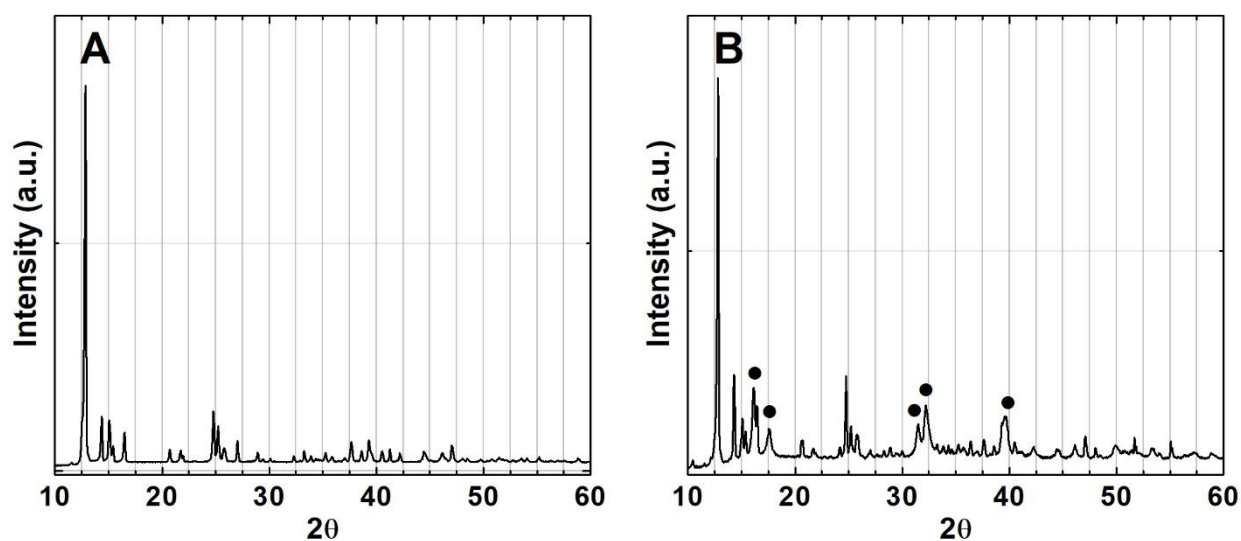


Figure S2 Representative diffraction patterns of **A)** group 1 with the detection of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, **B)** group 3 where $\text{Cu}_2(\text{OH})_3\text{Cl}$ (●) was detected together with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$; the identification of the copper oxalate was not possible by XRD most probably because it is in an amorphous form.

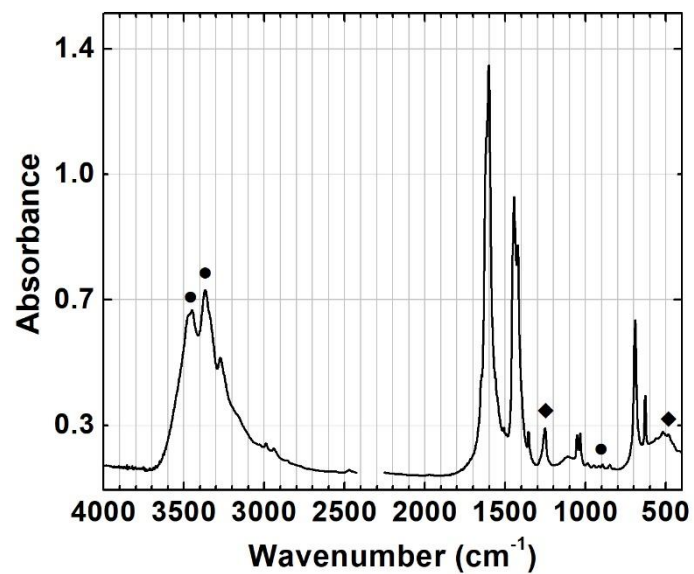










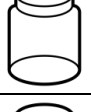


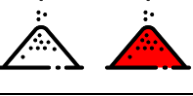
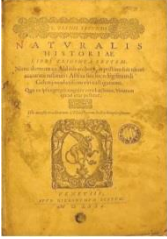
















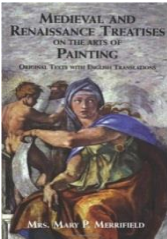
























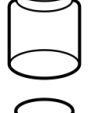


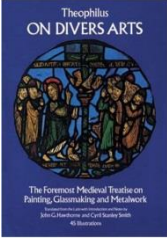













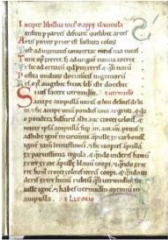

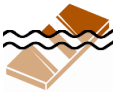




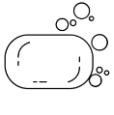
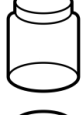
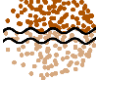


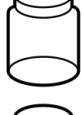



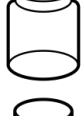


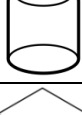


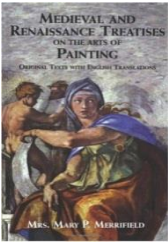




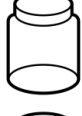


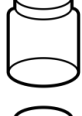


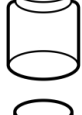


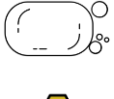
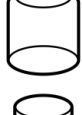



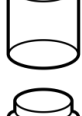


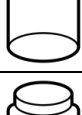


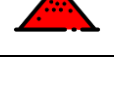

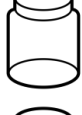


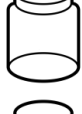



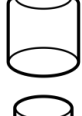



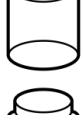


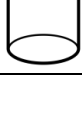


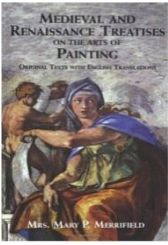




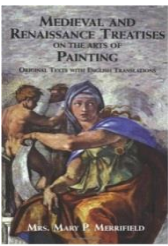
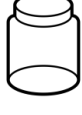


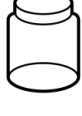





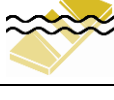


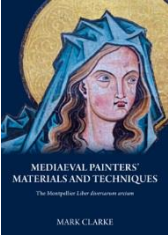












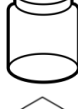




















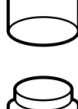











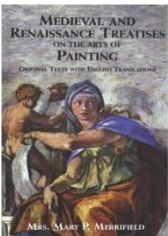






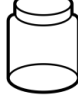


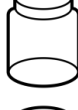



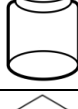



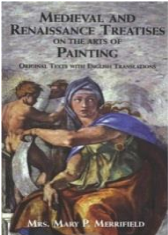






















Figure S3 Infrared spectrum of group 3 example where ammineite ($\text{CuCl}_2(\text{NH}_3)_2$) (◆) was detected together with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}_2(\text{OH})_3\text{Cl}$ (●).

Table S1 Written sources and specific recipes reproduced, together with a visual summary of the experimental set-up (see caption below the table) and final products. The main products formed are assembled in four groups; group 5 includes recipes in which no pigments were formed (unsuccessful).

TREATISES	RECIPE	CONTAINER	PRINCIPAL INGREDIENTS	ADDITIVES	GROUP	
 <i>De materia medica</i> Pedanio Dioscórides (I Century)	§ 5.79 "verdigris scraped (iós xystós)"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 5.79(2)(1) "verdigris scraped (iós xystós)"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 5.79(2)(2) "verdigris scraped (iós xystós)"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 5.79.6 "vermicular verdigris (skōlex iós)"					<i>no product</i>
 <i>Naturalis historia</i> Caio Plínio [Segundo] (I Century)	§ 34.26(1) "verdigris"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 34.26(2) "verdigris"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 34.26(3,4,5,6) "verdigris"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 34.26(3,4,5,6) (variation) "verdigris"				—	II Cu(CH ₃ COO) ₂ ·H ₂ O + CuC ₂ O ₄ ·nH ₂ O
	§ 34.28 "verdigris skolex"					<i>no product</i>
 <i>De coloribus et artibus romanorum</i> Eráclio & pseudo-Eráclio (VIII-XIII Century)	§ I.xi "green for writing"					<i>no product</i>
	§ III.XXXVIII "green of salt"					III Cu(CH ₃ COO) ₂ ·H ₂ O + Cu ₂ (OH) ₃ Cl + CuCl
	§ III.XXXVIII (variation) "green of salt"					I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ III.XXXVIII (variation) "green of salt"					III Cu(CH ₃ COO) ₂ ·H ₂ O + Cu ₂ (OH) ₃ Cl + CuCl
	§ III.XXXVIII (variation) "green of salt"					III Cu(CH ₃ COO) ₂ ·H ₂ O + Cu ₂ (OH) ₃ Cl + CuCl
	§ III.XXXVIII (variation) "green of salt"					I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ III.XXXIX "green"				—	II Cu(CH ₃ COO) ₂ ·H ₂ O + CuC ₂ O ₄ ·nH ₂ O
 <i>Schedula diversarum artium</i> Teófilo (XI-XII Century)	§ 35 "green of salt"					III Cu(CH ₃ COO) ₂ ·H ₂ O + Cu ₂ (OH) ₃ Cl + CuCl
	§ 36 "Spanish green"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 36 (variation) "Spanish green"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O
	§ 36 (variation) "Spanish green"				—	I Cu(CH ₃ COO) ₂ ·H ₂ O

TREATISES	RECIPE	CONTAINER	PRINCIPAL INGREDIENTS	ADDITIVES	GROUP
 <p>Mappae clavicula (IX-XII Century)</p>	§ v "Byzantine green"		 	-	II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ vi "Rouen green"		 		I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 80 "green"		 		IV NaCH_3COO + $\text{Cu}_2(\text{OH})_3\text{Cl}$ +
	§ 96 "green"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 106 "verdigris"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 221-D "verdigris"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
 <p><i>De coloribus faciendis</i> Pietro Di Sant Audemar (XIII-XIV Century)</p>	§ 151 "green of salt"		 		<i>no product</i>
	§ 152 "green"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 155 "Greek green"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 156 "Rothomagensian green"		 		<i>no product</i>
	§ 157 "verdigris for writing"		 		<i>no product</i>
	§ 159 "green"		 	-	<i>no product</i>
	§ 160 "verdigris"		 		<i>no product</i>
 <p><i>Liber de coloribus illuminatorum sive pictorum</i> (Ms. Sloane 1754) (XIV Century)</p>	p. 295 "verdigris"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	p. 295 "Rouen green"		 		<i>no product</i>
	p. 297 "green for writing (1)"		 		<i>no product</i>
	p. 297 "green for writing (2)"		 	-	II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	p. 303 "green"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
 <p><i>De diversis coloribus</i> Giovanni Alcherio (XIV-XV Century)</p>	§ 331 "green for writing"		 		<i>no product</i>
 <p><i>Experimenta de coloribus</i> Giovanni Alcherio (XV Century)</p>	§ 7-8 "green"		 	-	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 28 "green paint for writing"		 	 	<i>no product</i>
	§ 43 "verdigris"		 		IV <i>inconclusive</i>

TREATISES	RECIPE	CONTAINER	PRINCIPAL INGREDIENTS	ADDITIVES	GROUP
 <p><i>Liber diversarum arcium</i> (Ms. Montpellier) (XV Century)</p>	§ 1.16.2 "Greek green"		 	—	II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 1.16.3 "green of salt"		 	 	III $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{Cu}_2(\text{OH})_3\text{Cl} + \text{CuCl}$
	§ 1.16.4 "Rouen green"		 		<i>no product</i>
	§ 1.16.4 (variation) "Rouen green"		 		I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 1.16.5 "Spanish green"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 1.16.5 (variation) "Spanish green"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 1.16.5 (variation) "Spanish green"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 1.16.9 "flower of copper"		 	 	IV $\text{K}_2\text{SO}_4 + \text{Cu}_2(\text{OH})_3\text{Cl}$
	§ 1.16.10 "verdigris"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
§ 1.16.11-12 "Babylon green"		 		III $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{Cu}_2(\text{OH})_3\text{Cl} +$ $\text{CuCl}_2(\text{NH}_3)_2$	
 <p><i>O libro de como se fazen as cores</i> (XV Century)</p>	§ 11 "verdigris"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 12 "verdigris"		 		
 <p><i>Segreti per colori</i> (Ms. Bolonhês) (XV Century)</p>	§ 82 "verdigris"		 	—	<i>no product</i>
	§ 83 "verdigris"		 	—	II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 84 "verdigris"		 	—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	§ 85 "verdigris"		 		<i>no product</i>
	§ 95 "verdigris"		 		<i>no product</i>
 <p><i>Ricette per far ogni sorte di colori</i> (Ms. Pádua) (XVI-XVII Century)</p>	§ 130 "verdigris"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 130 (variation) "verdigris"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 130 (variation) "verdigris"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O} +$ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
	§ 130 (variation) "verdigris"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$
	§ 130 (variation) "verdigris"		 		II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $+ \text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$

TREATISES	RECIPE	CONTAINER	PRINCIPAL INGREDIENTS	ADDITIVES	GROUP
	§ 130 (variation) "verdigris"				II $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ + $\text{Na}_2\text{C}_2\text{O}_4$
 Filippe Nunes (XVII Century)	p. 122 "verdete (1)"			—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	p. 122 "verdete (2)"			—	I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
 (Ms. Bruxelles) Pierre Le Brun (XVII Century)	§ 10 "verdet"				<i>no product</i>
 Tratado de Barnices, y Charoles... (XVIII Century)	p. 87; p. 117 "vermicular verdigris"				<i>no product</i>
Other Experiments	verdigris with parchment glue				I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	verdigris with parchment glue				I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	verdigris with parchment glue and calcined salt				IV Cu acetates + Cu_2O + $\text{Cu}_2(\text{OH})_3\text{Cl}$ + CuCl
	verdigris with parchment glue and calcined salt				III $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{Cu}_2(\text{OH})_3\text{Cl}$ + CuCl
	verdigris with parchment glue and salt				I $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
	verdigris with parchment glue and salt				III $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ + $\text{Cu}_2(\text{OH})_3\text{Cl}$ + CuCl

LEGEND

CONTAINER	= oak	= glass	= metal	= oak (sealed with clay & covered with horse dung)
MODE	= suspension	= immersion	= sprinkler	
PRINCIPAL INGREDIENTS	= copper plate	= copper filings	= copper shavings	= commercial vinegar
	= brass plate	= brass filings	= handmade vinegar	= calucecumenon
ADDITIVES	= marine salt	= sal ammoniac	= honey	= parchment glue
	= calcined salt	= alumen	= soap	

= verdigris + calucecumenon