

1 Challenges in the characterisation of complex formulations of Asian lacquers from
2 museum objects by pyrolysis gas chromatography/mass spectrometry

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16

17 **Abstract**

18 A group of lacquered objects belonging to the Asian art collection of the Museum of
19 Zaragoza (Spain) were chemically studied with the aim to investigate the composition of
20 their coatings and possibly confirm their authenticity and geographical provenance.

21 Based on stylistic and art historical information, the objects are dated from the 16th to
22 the 20th century and are hypothetically produced in Japan, China, Myanmar and
23 Thailand.

24 Analytical pyrolysis with *in situ* silylation - gas chromatography coupled with mass
25 spectrometry (Py(HMDS)-GC/MS) was used to distinguish the various types of Asian
26 lacquers and identify additional original or restoration materials, by using a decisional
27 scheme based on the presence of characteristic pyrolytic profiles and molecular
28 markers. Scanning electron microscopy with energy-dispersive X-ray spectrometry
29 (SEM-EDS) was used on cross sections to study the stratigraphy of the objects and
30 understand the artistic techniques.

31 The results revealed a multifaceted picture, as some of the objects showed interesting
32 mixtures of lacquers, such as *urushi* and *thitsi*, or unexpected compositions, which
33 questioned their initial attributions. Complex or unexpectedly simple preparations and
34 restoration treatments of the decorative surfaces were highlighted too. The data are
35 here presented in a systematic way, showcasing the interest of these uncommon
36 analytical scenarios and the interpretational challenges provided by such complex
37 museum objects.

38

39 **Keywords:** Asian lacquers; analytical pyrolysis; *in situ* silylation; GC/MS; SEM-EDS;
40 provenance

41

42 1. INTRODUCTION

43 Asian lacquers have been used since ancient times in East Asia as coatings for all kinds
44 of surfaces, and lacquered objects have always been much-appreciated because of the
45 beauty, brightness, toughness, durability and waterproofing of their coatings [1, 2].

46 These objects and artworks are widespread in Oriental art, but they have also become
47 extremely popular in Europe since the 16th century [3], and have been collected since
48 then.

49 As far as museums are concerned, lacquered objects often enter the collections from
50 very diverse geographical regions and sometimes after multiple stops along the way.

51 Provenance is often attributed based on art historical knowledge, and, even when it is
52 officially recorded, debates and questions easily arise [4]. Given the popularity of
53 lacquered objects, European craftsmen started imitating and paraphrasing them, using
54 locally available materials and techniques to closely reproduce the glossy luxury of their
55 Oriental equivalents [5]. It is therefore extremely important to determine the
56 chronology, manufacture origin or even authenticity of such objects to avoid misleading
57 attributions [4].

58 The preparation of the lacquer coating is a complex process, in which mixtures of
59 several materials are used in multiple layers [6-8]. The complexity is enhanced by the
60 possible presence of additional substances, such as plant oils and pigments, used to
61 produce the lacquered decoration. The identification of all these materials is the first
62 crucial step to understand the overall composition of an object, solve problems of
63 conservation and authenticity, differentiate between the different Asian lacquers, point
64 towards provenance and distinguish European from Asian productions [9-11]. If the

65 exact preparation process and materials used are identified, hypotheses on specific
66 production centres are also possible [7].

67 The raw material of Oriental lacquerware is produced from the sap of three lacquer
68 trees: *Rhus vernicifera* (China, Japan and Korea), *Rhus succedanea* (Vietnam and
69 Taiwan), and *Melanorrhoea usitata* (Laos, Myanmar, Cambodia and Thailand) [12, 13].

70 Although the geographical distribution of these trees is a more complex topic than what
71 appears in the literature [14], the use of their sap is mostly reported in agreement with
72 the above-mentioned regions. The chemical composition of all saps is a complex
73 mixture of catechol and phenol derivatives (60–65%), proteins (glycoproteins (2%) and a
74 laccase enzyme (1%)), polysaccharides (7%) and water (30%) [15]. The laccase enzyme is
75 the responsible trigger for the polymerisation reaction that leads to the formation of
76 the hardened lacquer film [16]. The catechol/phenol mixture composition is different in
77 the three trees and such difference is maintained in the final polymer, thus enabling the
78 three types of lacquers to be chemically distinguished [17, 18]. The main components of
79 the product extracted from *Rhus vernicifera* are referred to as urushiol; laccol is
80 obtained from *Rhus succedanea*, and thitsiol from *Melanorrhoea usitata* [19]. Urushiol
81 and laccol main compounds are catechol derivatives with C15 and C17 alkenyl chain,
82 respectively. Thitsiol contains additional catechol derivatives with an ω -phenylalkyl
83 chain of C10 and C12 [15, 20].

84 Relatively abundant research has been undertaken to characterise Asian lacquers, by
85 focusing on finding molecular markers to identify the three different saps [21, 22],
86 studying the interactions between plant oils (used as additives in lacquer formulations)
87 and lacquers [23] and investigating the pathways of lacquer degradation [24, 25]. Due
88 to the high polymerisation degree and complex chemical composition of oriental

89 lacquers, pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS) is
90 the most suitable analytical approach for their chemical characterisation and for their
91 identification in samples of unknown composition [26-28]. Due to the high number of
92 pyrolysis products obtained and the difficulty of interpretation, a remarkable effort has
93 been made to systematise the identification process by using the AMDIS software in
94 combination with a complex Excel spreadsheet [27]. The polar nature of most pyrolysis
95 products derived from lacquer makes a derivatisation step highly recommended. Both
96 methylation (TMAH) [8, 9, 27] and silylation (HMDS) [15, 20] have been proposed in the
97 literature with good results. Advantages and disadvantages of these derivatisation
98 methods are mostly related to the identification of materials other than lacquer
99 possibly present in a sample, with TMAH being particularly suitable for lipids, and HMDS
100 being more suitable for proteins and polysaccharides [29]. Regardless of the
101 derivatisation method, the strategy to differentiate among lacquers is based on the
102 study of specific pyrolytic profiles and the identification of molecular markers [9, 12, 13,
103 15, 17, 20, 22, 26, 27, 30-33].

104 The study presented here was undertaken in order to delve into some significant
105 objects from the Asian art collection at the Museum of Zaragoza, Spain ("Federico
106 Torralba" collection) [34], with the aim to characterise the complex mixtures of
107 materials possibly present, assess the provenance of the objects and describe the
108 analytical difficulties arising from the study of these types of objects. To support and
109 guide the data interpretation, a simple decisional scheme was implemented, which was
110 then applied to the data obtained from the museum objects. Because many of the
111 lacquerwares were coloured or decorated, scanning electron microscopy (SEM) coupled
112 to energy-dispersive X-ray spectrometry (EDS) was used as complementary technique to

113 Py(HMDS)-GC/MS, in order to determine the elemental composition of the coatings and
114 study the artistic technique.

115

116 2. MATERIAL AND METHODS

117 2.1. Objects and samples

118 Eight lacquered objects were selected from the Asian art collection at the Museum of
119 Zaragoza (Spain). The objects include three food containers, three boxes, one plate and
120 one Buddha sculpture. They were selected in order to cover a chronological period from
121 the 16th to the 20th century and represent different possible provenances (China, Japan,
122 Myanmar and Thailand), according to stylistic interpretation. Table 1 includes an image
123 and a description of the objects under investigation. Some of these lacquerwares show
124 a European influence, as they were probably intended for the export market (49009,
125 49189 and 54562) and are referred to as *Nanban* art objects ¹ (49189 and 54562).

¹ This style was developed in Japan between the 16th and 17th centuries, and the word "*Nanban*" means "Southern barbarians", because it was linked to the contacts and trade with European people, especially from Portugal.

126 Table 1. Summary of the lacquered objects from the Asian art collection at the Museum of Zaragoza included in this research.

Museum code	Object	Description	Decoration	Chronology	Provenance	Size (l, w, h: cm)
49005		<i>Htamin-gyaing</i> (food container made of bamboo)	Black (exterior) and red (interior) lacquer; <i>kyaukka</i> decoration	First half of the 20 th century	Myanmar	23 (Ø), 48.5
49006		<i>Htamin-gyaing</i> (food container made of bamboo)	Red and black lacquer, with yellow, red and black decoration; <i>yun</i> (incised) technique	First half of the 20 th century	Myanmar	21.8 (Ø), 45
49188		Food container (basketry)	Black lacquer with red and gold decoration	First half of the 20 th century	Thailand or Myanmar	29.5 (Ø), 39
49189		Nanban <i>yōhitsu</i> (small chest)	Black lacquer with <i>maki-e</i> and <i>raden</i> decoration	End of the Momoyama period or beginning of the Edo era, 17 th century	Japan	45.2, 24.9, 29.5

54562		Nanban <i>yōdansu</i> (writing box)	Black lacquer with red, <i>maki-e</i> and <i>raden</i> decoration	Momoyama period, end of the 16 th century or beginning of the 17 th century	Japan	25.4, 25.5, 23.3
48990		Amida-Buddha	Gilded decoration	Edo period, 19 th century	Japan	23.5, 12.5, 56.5
48165		Sewing box	Brown lacquer with golden decoration	First half of the 19 th century	China	63.7, 43.7, 71
49009		Plate	Non-shinning red lacquer with golden and black decoration	Qing period, 18 th century or beginning of the 19 th c.	China	25.2 (Ø), 4.8

127 Two sets of micro-samples (with total diameter less than 1 mm) were taken from all the
128 objects by using a scalpel and then stored in glass vials. To minimise sampling of these
129 precious objects, one set of micro-samples was used for SEM-EDS examination and the
130 other one for Py(HMDS)-GC/MS. Monochrome and non-decorated micro-samples were
131 mainly used for Py(HMDS)-GC/MS analyses, and coloured micro-samples were selected
132 for SEM-EDS.

133

134 2.2. Py(HMDS)-GC/MS

135 Analytical pyrolysis was performed using 1,1,1,3,3,3-hexamethyldisilazane (HMDS,
136 chemical purity 99.9%, SigmaAldrich Inc., USA) as a silylating agent for the *in situ*
137 derivatisation of pyrolysis products. The instrumentation consisted of a micro-furnace
138 Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab) coupled to a gas chromatograph
139 6890 (Agilent Technologies, Palo Alto, CA, USA), equipped with an HP-5MS fused silica
140 capillary column (stationary phase 5% diphenyl and 95% dimethyl-polysiloxane, 30 m ×
141 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m ×
142 0.32 mm i.d., Agilent J&W, USA). The GC instrument was coupled to an Agilent 5973
143 Mass Selective Detector operating in electron impact mode (EI) at 70 eV. The micro-
144 sample (*ca.* 100 µg) was admixed with 3 µL HMDS into a stainless steel cup and inserted
145 into the micro-furnace. The pyrolysis temperature was 550°C and interface temperature
146 was 280°C. The split/splitless injector was used with a 1:20 split ratio and kept at 280°C.
147 Chromatographic conditions were as follows: initial temperature 36°C, 10 min
148 isothermal; 10°C min⁻¹ up to 280°C, 2 min isothermal; 20°C min⁻¹ up to 310°C, 50 min
149 isothermal. Helium (purity 99.995%) was used as carrier gas with constant flow 1.0 mL
150 min⁻¹.

151

152 **2.3. SEM-EDS**

153 The observations and analyses were obtained by Field-Emission Scanning Electron
154 Microscopy (FESEM) with Energy-Dispersive X-ray Spectrometry (EDS); they were
155 performed with a Merlin™ FESEM microscope equipped with a Gemini column (both
156 from Carl Zeiss Nano Technology Systems, Germany), and coupled with an X-Max X-ray
157 microanalyzer (Oxford Instruments, UK). Cross-sections of the micro-samples were
158 prepared by embedding them in epoxy resin, polished with diamond polishing
159 suspensions, coated with carbon and fixed to the FESEM holder. The FESEM
160 observations and EDS analyses were performed at 15.0 kV and 300 pA.

161 Polished cross-sections were previously observed by Optical Microscopy (OM) using a
162 Zeiss Axio Imager Reflected-light Microscope (Carl Zeiss, Jena, Germany) with polarised
163 light.

164

165 **3. RESULTS AND DISCUSSION**166 *Data analysis*

167 The pyrolysis data were interrogated with the aim to highlight pyrolytic profiles and
168 molecular markers based on what is reported in the literature [9, 12, 13, 15, 17, 20, 22,
169 26, 27, 30-33]. A summary of these profiles and markers is reported in Table 2, together
170 with the mass-to-charge (m/z) values used to extract chromatographic profiles of non-
171 derivatised compounds, as well as methylated and silylated derivatives.

172 **Table 2.** Summary of pyrolytic profiles and molecular markers commonly used in the literature to distinguish Asian lacquers [9, 12, 13, 15, 17, 20,
 173 22, 26, 27, 30-33]. The *m/z* values of the ions used to extract them are reported together with additional description of the profiles obtained. The
 174 classes of compounds are indicated with abbreviations: C – aliphatic hydrocarbons; B – alkylbenzenes; Ph – alkylphenols; Ct – alkylcatechols; ωPh
 175 – ω-alkylphenylphenols; ωCt – ω-alkylphenylcatechols; K – alkylphenylketones; Ct_{ox} – acid alkylcatechols; Ph-A – alkylphenyl carboxylic acids; Ox-
 176 A – alkyl-oxo-phenylcarboxylic acids. The carbon atoms in the alkyl chains and the unsaturations are indicated with numbers: C_n:_m – n=number
 177 of carbon atoms; m=number of unsaturations.

	<i>m/z</i>	<i>Urushi</i>	<i>Laccol</i>	<i>Thitsi</i>	Comment
Pyrolytic profiles					
Aliphatic hydrocarbons (C)	55 (alkenes)	Present from C9:1 to C15:1, peaking at C14:1	Present from C9:1 to C17:1, peaking at C16:1	Present from C9:1 to C17:1, with C14:1 as most abundant	<i>Thitsi</i> is difficult to identify based only on C profiles
	57 (alkanes)	Present from C9 to C15, peaking at C15	Present from C9 to C17, peaking at C17	Present from C9 to C17, peaking at C15	
Alkylbenzenes (B)	91	Decreasing profile from B1 to B9-B10	Decreasing profile from B1 to B11-B12	Gaussian profile from B1 to B12, peaking at B11:1	The B profile of <i>thitsi</i> is highly distinctive
Alkylphenols (Ph)	108	Gaussian profile from	Gaussian profile from Ph1 to Ph17,	Complex profile from Ph1 to Ph17 with	All profiles are highly distinctive
	122 (Me)*				

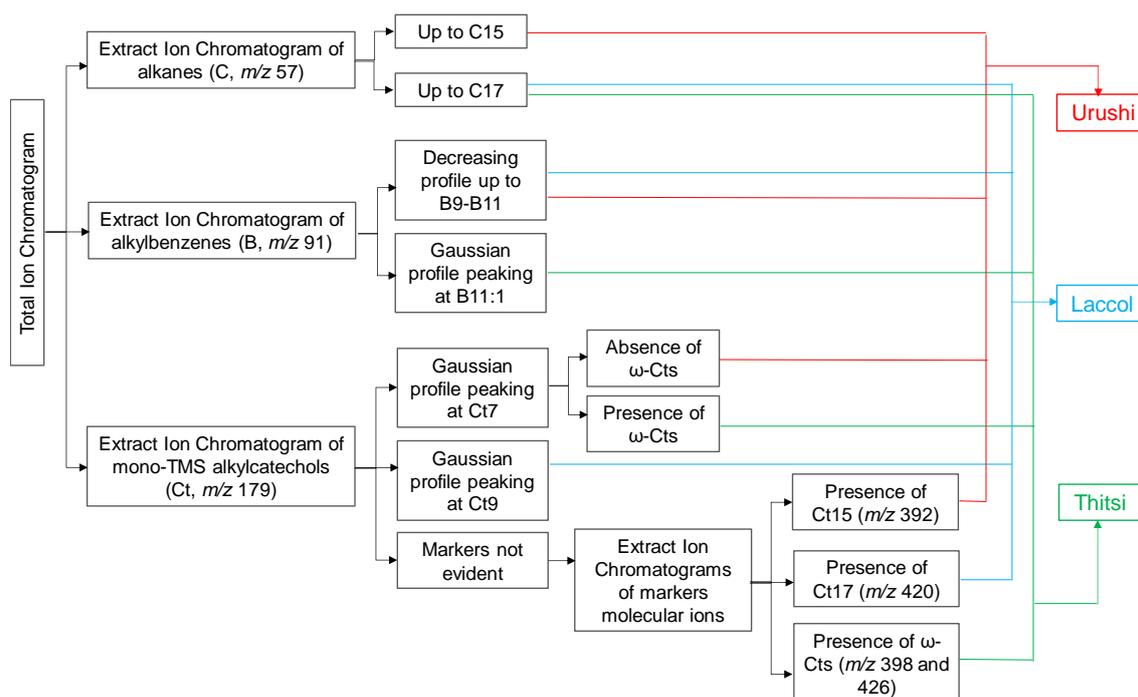
	180 (TMS)**	Ph1 to Ph15, peaking at Ph7	peaking at Ph9	additional presence of ω Ph10 and ω Ph12	
Alkylcatechols (Ct)	123	Gaussian profile from Ct1 to Ct15, peaking at Ct7	Gaussian profile from Ct1 to Ct17, peaking at Ct9	Complex profile from Ct1 to Ct17 with additional presence of ω Ct10 and ω Ct12	The profile of disilylated catechols is sometimes more complicated, as it is dependent on steric hindrance issues during the derivatisation process
	151 (Me)				
	179 (TMS)				
	253-267 (2TMS)				
Molecular markers					
Ph15:1	302	Present	Present	Present	
	316 (Me)				
	374 (TMS)				
Ph15	304	Present	Present	Present	
	318 (Me)				
	376 (TMS)				
Ct15:1	318	Present	Present	Present	
	346 (Me)				
	390 (TMS)				
	462 (2TMS)				
Ct15	320	Present	Present	Present	
	348 (Me)				
	392 (TMS)				
	464 (2TMS)				
Ph17:1	330	Absent	Present	Present	
	344 (Me)				
	402 (TMS)				
Ph17	332	Absent	Present	Present	
	346 (Me)				

	404 (TMS)				
Ct17:1	346	Absent	Present	Present	
	374 (Me)				
	418 (TMS)				
	490 (2TMS)				
Ct17	348	Absent	Present	Present	
	376 (Me)				
	420 (TMS)				
	492 (2TMS)				
ω Ph10	310	Absent	Absent	Present	
	324 (Me)				
	382 (TMS)				
ω Ct10	326	Absent	Absent	Present	
	354 (Me)				
	398 (TMS)				
	470 (2TMS)				
ω Ph12	338	Absent	Absent	Present	
	352 (Me)				
	410 (TMS)				
ω Ct12	354	Absent	Absent	Present	
	382 (Me)				
	426 (TMS)				
	498 (2TMS)				
Degradation products					
Acid alkylcatechols (Ct _{ox})	123	Present from Ct _{ox} 6 to Ct _{ox} 9, peaking at Ct _{ox} 8	Present from Ct _{ox} 7 to Ct _{ox} 12, peaking at Ct _{ox} 10	Ct _{ox} 8 generally present as most abundant	
	151 (Me)				
	179 (TMS)				

Alkylphenylketones (K)	105	Not present	Not present	Gaussian profile from K1 to K12, peaking at K11:1	They are considered degradation products, but they appear in relative fresh <i>thitsi</i> as well
Alkylphenyl carboxylic acids (Ph-A)	91	Not present	Not present	Gaussian profile from Ph-A10 to Ph-A14, peaking at Ph-A12 and Ph-A13	
Alkyl-oxo-phenylcarboxylic acids (Ox-A)	105	Not present	Not present	Gaussian profile from Ox-A10 to Ox-A14, peaking at Ox-A12 and Ox-A13	

178 * methylated - **trimethylsilylated

179 Based on previous published research, as well as on the experience of the authors, a
 180 decisional scheme was implemented and is reported in Figure 1. The scheme shows the
 181 m/z values for silylated compounds, but it can be used in the case of methylation or
 182 non-derivatised compounds by using the m/z values reported in Table 2.
 183



184

185 **Figure 1.** Proposed decisional scheme for the differentiation of *urushi*, laccol and *thitsi*
 186 using Py(HMDS)-GC/MS. Further confirmation of identification is then obtained by
 187 extracting the profiles of alkylphenols (Ph, m/z 180) and bis-TMS alkylcatechols (m/z
 188 253) in the same way proposed for mono-TMS alkylcatechols. The corresponding m/z
 189 values for these additional profiles are reported in Table 2.

190

191 FESEM-EDS results were used to distinguish decoration layers and microstructure, and
 192 to identify the pigments, in order to improve the knowledge of the lacquer artistic
 193 techniques.

194 In the following paragraphs, the results are presented according to the area of
195 provenance of the objects.

196

197 *Objects 49005, 49006 and 49188 – food containers, Myanmar and Thailand, early 20th*
198 *century*

199 The total ion chromatograms (TICs) of the samples taken from objects 49005 and 49006
200 are similar (Figure 2a), and show the whole molecular pattern generally reported for
201 *thitsi* [24], including the distinctive profile of alkylbenzenes (B, m/z 91, Figure 2b) and
202 alkylphenylketones (K, m/z 105, not shown).

203 The profile of alkylcatechols (Ct, m/z 179, Figure 2c) is more complex but still contains
204 all the features expected for *thitsi*, including the molecular markers, such as 3-(10-
205 phenyldecyl)catechol (ω Ct10) and 3-(12-phenyldodecyl)catechol (ω Ct12), despite their
206 low relative abundance. A more successful visualisation of the molecular markers was
207 generally obtained by directly extracting the m/z values corresponding to their
208 molecular ions (Table 2). A cleaner profile was obtained from the alkylphenols (Ph, m/z
209 180, not shown), showing the typical Gaussian profile and the molecular markers 2- and
210 3-(10-phenyldecyl)phenols (ω Ph10), and 2- and 3-(12-phenyldodecyl)phenols (ω Ph12).

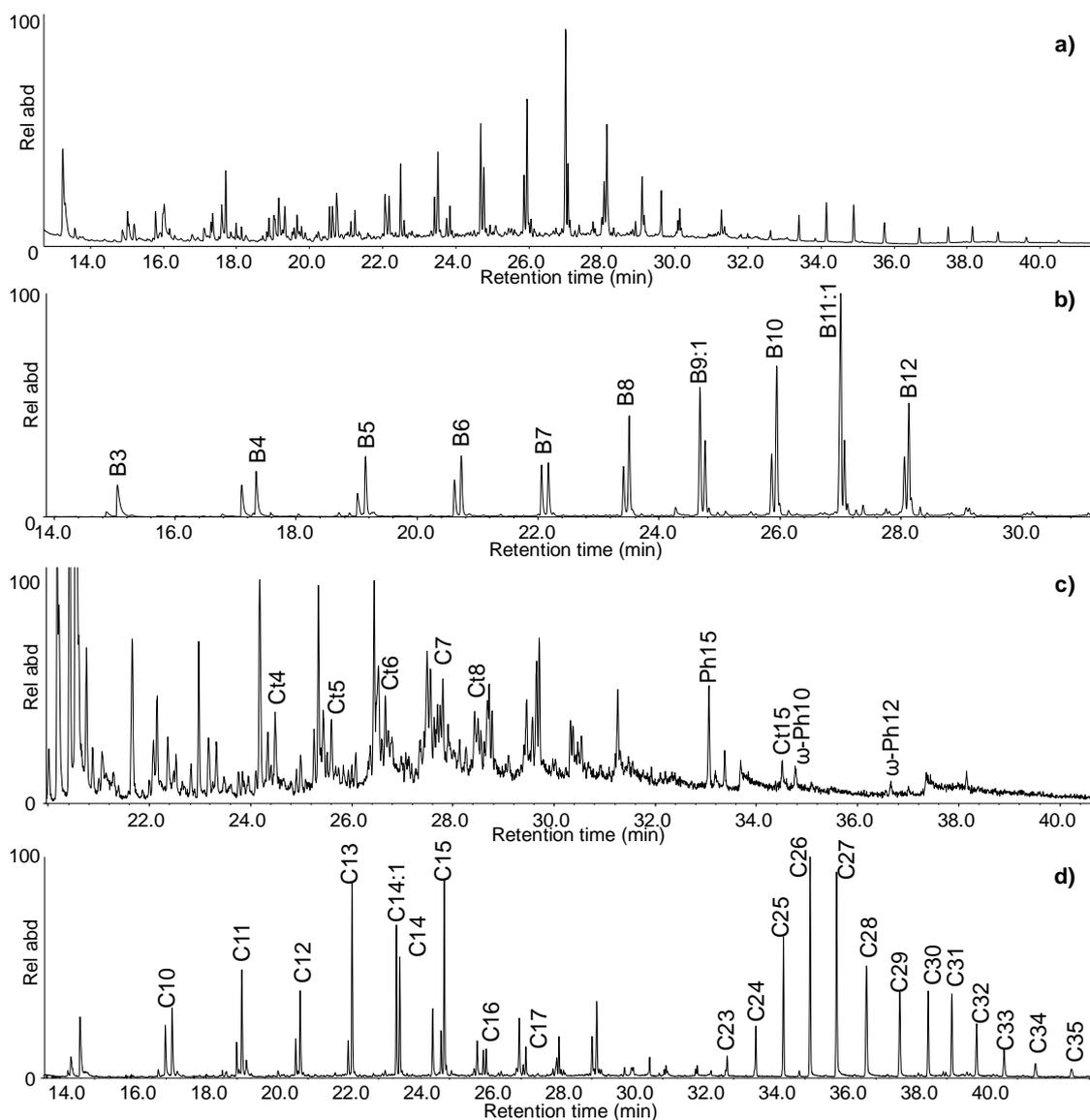
211 The first part of the pyrolytic profile of aliphatic hydrocarbons (C, m/z 57, Figure 2d)
212 shows saturated and unsaturated compounds up to C17, in accordance with the
213 composition of *thitsi*, which naturally contains alkylcatechols with up to 17 carbon
214 atoms. All these features satisfy the steps described in the decisional scheme reported
215 in Figure 1 for the straightforward identification of *thitsi*. However, at higher retention
216 times, longer-chain aliphatic hydrocarbons (C23-C35) are present. The Gaussian shape
217 of the profile and the distribution of the hydrocarbons is in good agreement with the

218 presence of paraffin wax [35]. There is no record of paraffin wax used in the traditional
219 preparation of *thitsi* [7], suggesting that this material most likely belongs to a past
220 conservation treatment.

221 Other materials are commonly found mixed with lacquer, including oils, proteins and
222 sugars [27, 36, 37]. No molecular markers for these materials were identified in sample
223 49006, whereas some markers for lipids were detected in sample 49005, in particular
224 nonandioic acid (azelaic acid), thus suggesting the presence of a drying or semi-drying
225 oil, which is commonly added to Asian lacquer formulations [7, 24, 27].

226 These results confirm the Southeast Asian provenance of both objects, as relatively pure
227 *thitsi* appeared to be applied on their surfaces, in agreement with traditional practice in
228 Myanmar.

229



230

231 **Figure 2.** Chromatographic profiles obtained by Py(HMDS)–GC/MS of sample 49006. **a)**232 Total ion chromatogram; **b)** extracted ion chromatogram (m/z 91), showing B3)

233 propylbenzene, B4) butylbenzene, B5) pentylbenzene, B6) hexylbenzene, B7)

234 heptylbenzene, B8) octylbenzene, B9:1) nonenylbenzene, B10) decylbenzene, B11:1)

235 undecenylbenzene, B12) dodecylbenzene, **c)** extracted ion chromatogram (m/z 179),

236 showing Ct4) 3-butylcatechol (TMS), Ct5) 3-pentylcatechol (TMS), Ct6) 3-hexylcatechol

237 (TMS), Ct7) 3-heptylcatechol (TMS), Ct8) 3-octylcatechol (TMS), Ph15) 3-

238 pentadecylphenol (TMS), Ct15) 3-pentadecylcatechol (TMS), ωPh10) 3-(10-

239 phenyldecyl)phenol, ωPh12) 3-(12-phenyldodecyl)phenol; **d**) extracted ion
240 chromatogram (m/z 57), showing C10) decane, C11) undecane, C12) dodecane, C13)
241 tridecane, C14:1) tetradecene, C14) tetradecane, C15) pentadecane, C16) hexadecane,
242 C17) heptadecane, C23) tricosane, C24) tetracosane, C25) pentacosane, C26)
243 hexacosane, C27) heptacosane, C28) octacosane, C29) nonacosane, C30) triacontane,
244 C31) hentriacontane, C32) dotriacontane, C33) tritriacontane, C34) tetratriacontane,
245 C35) pentatriacontane.

246

247 Another food container (object 49188), supposedly from Thailand, was present among
248 the objects under investigation. The TIC does not present the typical pyrolytic profile of
249 *thitsi*, which would be expected in the case of a Thai lacquered object. A series of
250 compounds not related to the presence of an Asian lacquer were identified (Figure S1a,
251 Supplementary Information), including, short-chain aliphatic carboxylic acids, glycerol,
252 phthalic anhydride, several phthalates, ethylene and diethylene glycols and
253 polysaccharide pyrolysis products. These last compounds (mostly levoglucosan
254 derivatives) might indicate the presence of a cellulose- or starch-based material, but
255 contamination from the wooden support cannot be excluded. Short-chain aliphatic
256 carboxylic acids, as well as small amounts of palmitic and stearic acids, suggest the
257 presence of a lipid material. Phthalic anhydride, phthalates and glycerol were also
258 detected in the same sample. These are known additives in alkyd resin formulations
259 [38], which are modified drying oils [39]. The lack of a pyrolytic profile of carboxylic
260 acids similar to the ones normally obtained for drying oils (presence of azelaic acid and
261 high relative abundance of palmitic and stearic acids [40]) makes the identification of
262 the lipid material uncertain. Nonetheless, it has to be noted that the derivatisation of

263 the sample was not completely successful. Additionally, the presence of a broad tailed
264 chromatographic peak at 21.35 min, whose mass spectrum showed the isotopic pattern
265 of Hg, was highlighted. This is reported in the literature as indicative of the presence of
266 vermillion (HgS) [41]. As the derivatisation reaction is generally affected by the presence
267 of inorganic compounds, it is possible that the carboxylic acid profile was consequently
268 affected, not allowing the straightforward identification of the alkyd resin.

269 The TIC also shows long-chain aliphatic hydrocarbons indicative of the presence of a
270 mineral wax, but the distribution of the hydrocarbons is different compared to the
271 paraffin wax identified in the two samples previously discussed. However, the profile is
272 still consistent with reported paraffin waxes recovered from various petroleum
273 products [35].

274 Despite the predominance of peaks not related to lacquer in the TIC, the use of extract
275 ion chromatograms (EICs), as specified in the scheme of Figure 1, enabled the presence
276 of *thitsi* to be assessed. In particular, the pyrolytic profile of aliphatic hydrocarbons (C,
277 m/z 57, Figure S1d, Supplementary Information) is in good agreement with the general
278 profile of *thitsi* and similar to those obtained for objects 49005 and 49006. The pyrolytic
279 profile of alkylphenols (Ph, m/z 180, Figure S1c, Supplementary Information) also shows
280 several compounds, with Ph7 as the most abundant one and with ω Ph10 and ω Ph12
281 clearly detectable in the profile. Surprisingly, the pyrolytic profile of alkylbenzenes (B,
282 m/z 91, Figure S1b, Supplementary Information) did not show the typical Gaussian
283 profile of *thitsi*, which is considered one of the most reliable features to identify the
284 lacquer. Ageing, or possibly interactions with other materials, might have affected the
285 lacquer molecular composition, or pyrolytic behaviour. This result is important because
286 it shows how complex the interpretation of the results can be when additional materials

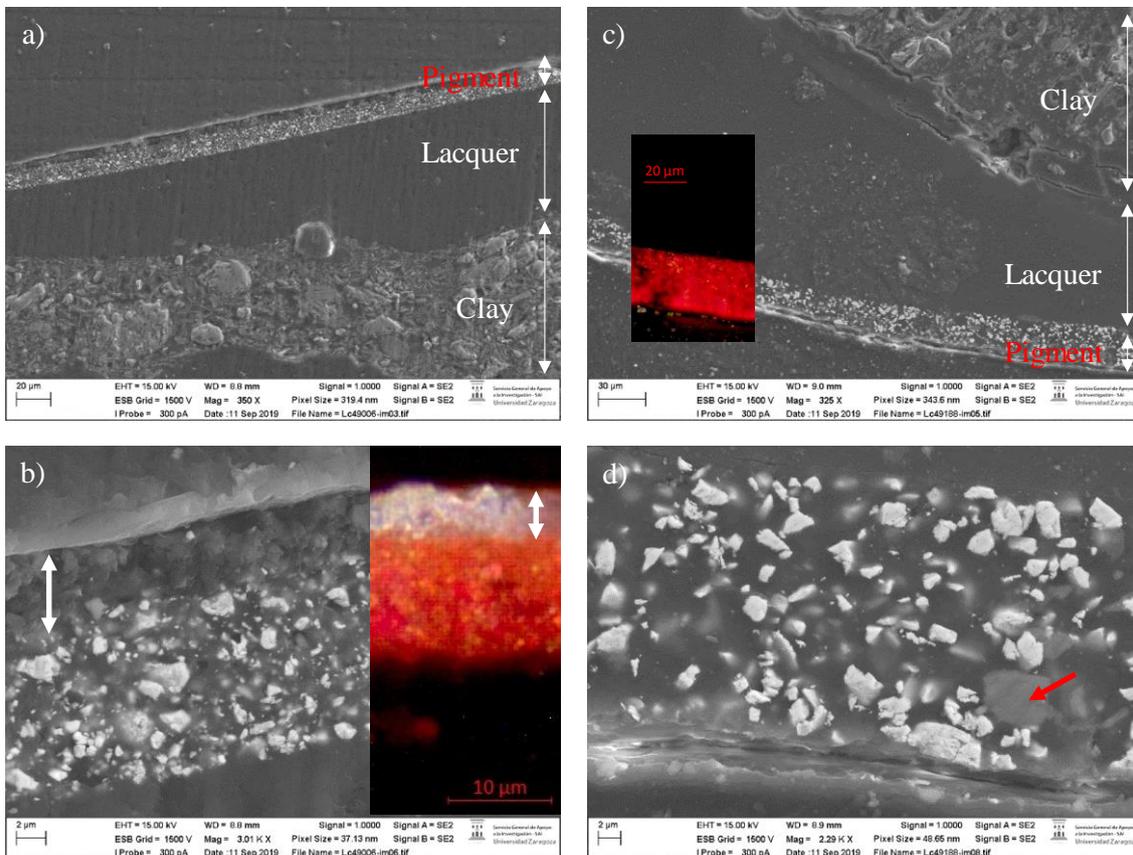
287 from restoration are present in the same sample. Nevertheless, the identification of
288 *thitsi* based on the molecular markers is solid and the provenance of the object is thus
289 confirmed.

290 The cross sections of samples from objects 49006 and 49188 were studied by FESEM-
291 EDS (Figure 3). The decoration of lacquered objects is a complex process, which requires
292 the application of several layers [1]. In the case of these objects, the wooden support
293 was coated with a clayey powder, a process referred to as *shitachi* (surface treatment in
294 Japanese) or, more appropriately *thayo* ground, for Burmese objects. This clayey layer
295 was sealed with a layer of black lacquer about 50-80 μm thick (Figures 3a and 3c), which
296 usually constitutes the finished ground for further decoration. The coloured layer was in
297 fact applied on the top of the black lacquer layer.

298 In the case of sample 49006, the red colour was obtained by vermilion (HgS) mixed with
299 lacquer, resulting in a layer about 10 μm thick (Figures 3a and 3b). Most of the HgS
300 particles are less than 1 μm long. An additional top layer is also clearly present (Figure
301 3b, marked with an arrow), about 3-4 μm thick, whitish in colour in OM (Figure 3b). The
302 inorganic elemental composition, as determined by EDS, showed the presence of Si, Al
303 and some other minor elements, which suggest an environmental contamination. The
304 layer, mostly organic, might therefore correspond to an original finishing layer or a
305 protective layer applied during a conservation treatment. Nonetheless, the stratigraphic
306 analysis matched the visual observations and decoration design, thus confirming the
307 object to be traditionally decorated using the *yun* (incised) technique [7]. In the case of
308 sample 49188, the red layer (Figures 3c and 3d), whose thickness is around 15 μm , was
309 prepared using vermilion (HgS), with the addition of gypsum (calcium sulphate, CaSO_4).
310 Ca, S and O were detected by EDS and gypsum particles are marked with an arrow in

311 Figure 3d. The HgS particles are averagely about 2 μm long (slightly bigger than for
 312 object 49006) and traces of iron oxides were also detected.

313



314

315 **Figure 3.** Images obtained by FESEM of the cross-sections of samples: **a)** 49006,
 316 secondary electron (SE) image showing the whole stratigraphy; **b)** 49006, SE image of
 317 the pigment at the surface (white particles in the image) and optical photomicrograph
 318 of the top layer; **c)** 49188, SE image showing the whole stratigraphy and optical
 319 photomicrograph of the top layer; **d)** 49188, SE image of the red pigment (white
 320 particles in the image; arrow marks a calcium sulphate inclusion, in grey).

321

322 *Objects 49189 and 54562 – boxes, Japan, 16th-17th century – and object 48990 - Buddha*
 323 *sculpture, Japan, early 19th century*

324

325 The two boxes are considered the oldest examples among the items selected for this
326 study and they are supposed to be made in Japan, possibly for the export market.

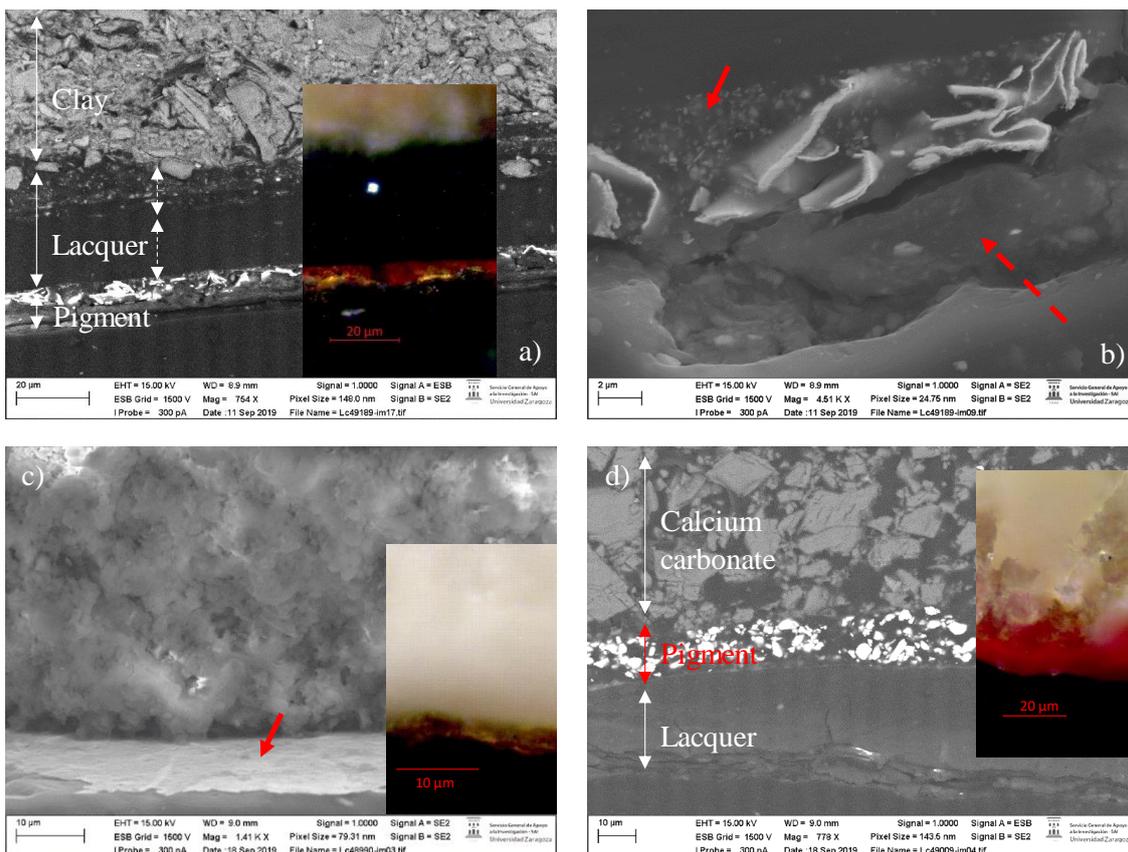
327 In the case of object 49189, the TIC shows the presence of aliphatic carboxylic acids
328 among the most abundant pyrolysis products (Figure S2a, Supplementary Information).

329 It has been proved in a previous study that, when a drying oil is mixed with *urushi*, the
330 curing of the two materials is mutually affected [23]. In particular, the pyrolytic profile
331 of the oil shows short-chain aliphatic carboxylic acids (C5-C9) with high relative
332 abundance and azelaic acid (diC9) is present with lower relative abundance compared
333 to a drying oil curing on its own. The results from this sample were in perfect agreement
334 with these observations, thus suggesting the presence of a drying oil mixed with an
335 Oriental lacquer. Additionally, a series of sesquiterpenes including cedrene, cuparene,
336 cadalene and mayurone were identified. These compounds are all present in essential
337 oils extracted from trees of the *Cupressaceae* family and are reported as possible
338 additives during the preparation of *urushi* lacquer [27].

339 The presence of the lacquer was assessed by using the EICs, following the steps
340 described for *urushi* in Figure 1. In particular, the alkylbenzenes (B, m/z 91, Figure S2b,
341 Supplementary Information) show homologues up to nonylbenzene (B9); the
342 alkylcatechols (Ct, m/z 179, Figure S2c, Supplementary Information) show that the most
343 abundant peak is the one attributed to 3-heptylcatechol (Ct7), and the aliphatic
344 hydrocarbons (C, m/z 57, Figure S2d, Supplementary Information) show tetradecene
345 (C14:1) and pentadecane (C15) as the most abundant homologues. 3-
346 pentadecylcatechol (Ct15) and 3-pentadecylphenol (Ph15) are present with very low
347 relative abundance, but still detectable, especially visible extracting the m/z values
348 corresponding to their molecular weights (Table 2). These results enabled *urushi* to be

349 identified as the Asian lacquer used to decorate this object. Paraffin wax was also
350 present in the sample, as previously observed in other objects.

351 A cross-section of sample 49189 was observed by FESEM-EDS. This micro-fragment
352 corresponds to a decorated surface in black with gold powder (*maki-e* decoration). A
353 layered structure is observed (Figure 4a), but this is more complex compared to the
354 Burmese samples. The ground layer is a clayey coating, as identified by elemental
355 analysis by EDS, with some inclusions composed of Ca, S and O, and sealed by the
356 lacquer (Figures 4a and 4b). Two different sub-layers of lacquer can be distinguished
357 (Figure 4a, marked with dashed arrows). The first one shows an irregular thickness of 5-
358 15 μm and the lacquer is mixed with a finely ground powder, following the typical
359 Japanese *shitachi* process. The second sub-layer is about 20 μm thick. This layer was
360 probably smoothed and polished. The outer coating (about 5 μm thick) corresponds to
361 the decoration and is composed of golden particles in a red layer. The pigment used is
362 an extremely fine iron oxide powder (Figure 4b, plain arrow) and a lacquer/oil mixture
363 was probably used as adhesive. The chemical composition of the metal particles is gold,
364 with traces of silver, and they are less than 10 μm long and extremely thin (see Figure
365 4b). On the top of the golden design, along the cross-section surface, a final layer is
366 observed, composed of C, O, Ca, and others (Figure 4b, dashed arrow). According to the
367 *shitachi* process, after the final lacquer polishing, a last coating with at least three fine
368 lacquer layers is applied, although some sophisticated lacquerwares could be painted
369 with dozens of layers of lacquer coatings [1]. All these observations were consistent
370 with the *maki-e* decoration technique, which is a very traditional and widespread type
371 of sprinkled-gold design commonly seen on Japanese lacquer objects [42].
372



373

374 **Figure 4.** Images obtained by FESEM of the cross-sections of samples: **a)** 49189,
 375 backscattering electron (BSE) image showing the whole stratigraphy and an optical
 376 photomicrograph of the top layer; **b)** 49189, secondary electron (SE) image of the
 377 surface decoration (plain arrow indicates iron oxide particles and dashed arrow marks
 378 the top upper layer); **c)** 48990, SE image and optical photomicrograph showing a
 379 decoration made of bone or ivory on the top (Ca, P and O detected by EDS) and with
 380 arrow pointing to the gold foil on the lacquer; **d)** 49009, BSE image showing the whole
 381 stratigraphy and optical photomicrograph of the red layer.

382

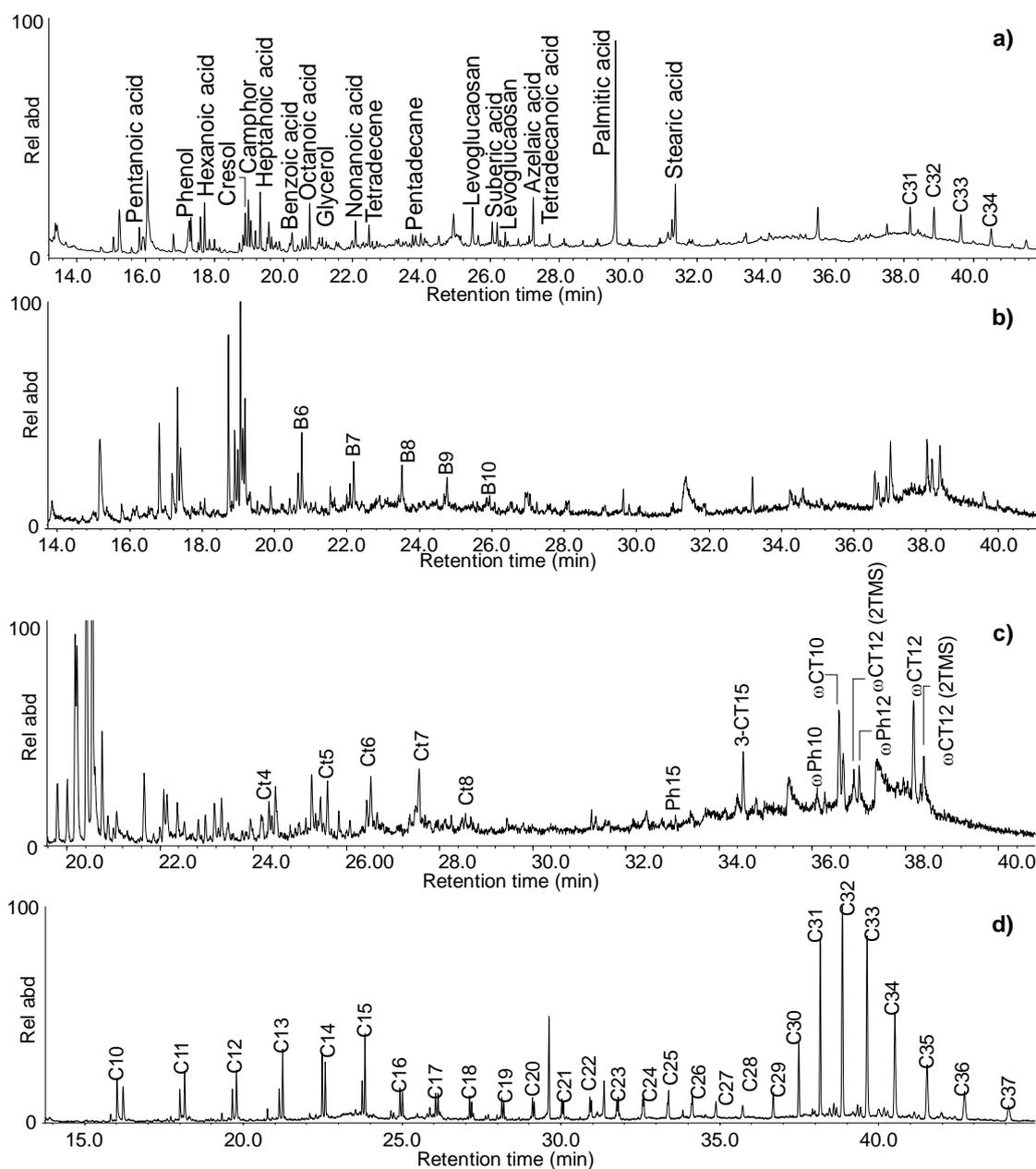
383 In the case of object 54562, the TIC (Figure 5a) shows the presence of aliphatic
 384 carboxylic acids with a similar distribution to that observed for object 49819, therefore
 385 indicating the use of a drying oil. Camphor was identified, which is another known

386 additive of *urushi* formulations [27]. A paraffin wax was also present, as suggested by
387 the presence and distribution of long-chain aliphatic hydrocarbons, as previously
388 discussed.

389 The EIC of the alkylbenzenes (Figure 5b) is in agreement with the profile reported for
390 *urushi*, but the EIC of the alkylcatechols (Figure 5c) clearly shows the presence of all the
391 *thitsi* markers, thus placing the sample in none of the scenarios shown in the decisional
392 scheme of Figure 1. In the case of this sample, the profile of hydrocarbons (Figure 5d)
393 was not useful to distinguish between *urushi* and *thitsi*, as these compounds overlap
394 with the ones deriving from the paraffin wax. Overall, the lack of the alkylbenzenes
395 typical of *thitsi* together with the presence of *thitsi* molecular markers makes the
396 interpretation of the results challenging. A mixture of *urushi* and *thitsi* is the most likely
397 hypothesis, but it is difficult to ascertain whether this mixture was originally used to
398 decorate the object or is the result of a later addition. The design of the box definitely
399 places it as a Japanese object, but it is suspected to be made for the export market. The
400 use of *thitsi* imported to Japan and used in mixture with *urushi* for Japanese export
401 lacquer is reported since the 17th century [35]. This object could therefore be one of the
402 few scientifically-confirmed examples of this practice. In the hypothesis of an original
403 mixture of *urushi* and *thitsi*, it is reasonable to think that the two lacquers mixed
404 together would polymerise differently than when they polymerise separately. In
405 particular, *urushi* forms C-C aromatic nucleus-side chain coupling bonds, C-O phenolic
406 oxygen-side chain coupling bonds and C-C bonds between side chains [43], whereas in
407 *thitsi* nuclear-nuclear C-C couplings are predominant [44]. A co-polymerisation would
408 therefore affect the distribution of dimeric bonds and consequently the pyrolytic

409 profiles, possibly justifying the profile of alkylbenzenes obtained. This would be an
 410 interesting area for future research.

411



412

413 **Figure 5.** Chromatographic profiles obtained by Py(HMDS)–GC–MS of sample 54562. **a)**

414 Total ion chromatogram; **b)** extracted ion chromatogram (m/z 91); **c)** extracted ion

415 chromatogram (m/z 179); **d)** extracted ion chromatogram (m/z 57). Refer to Figure 2

416 and Table 2 for labels.

417

418 The Buddha sculpture (object 48990) is described as produced in Japan in the early 19th
419 century. However, a mixture of drying oil and *thitsi* was clearly identified. All the
420 extracted ion chromatograms matched with the profiles expected for this lacquer, in
421 agreement with the scheme in Figure 1, therefore strongly questioning the Japanese
422 origin of this object. In the case of a real Japanese production, this object would have
423 probably been made for the export market in a similar way to object 54562, but using
424 pure *thitsi*, which was less expensive than *urushi*. However, furniture and boxes were
425 dominating the export market in the 19th century, whereas a Buddha sculpture would
426 have been less attractive for European customers, strengthening a possible Southeast
427 Asian origin of the object.

428 The results of sample 48990 by FESEM-EDS may also support a possible Burmese or Thai
429 manufacture, because a decoration with a last coating of extremely thin gold foil is
430 observed. This finishing is typical of lacquerware from Myanmar (Figure 4c) and is
431 referred to as *shwe zawa* [24]. The object is also decorated with bone or ivory, and this
432 material was confirmed by the detection of Ca, P and O by EDS analysis in the layer
433 above the gold foil (Figure 4c, top).

434

435 ***Objects 49009 (plate) and 48165 (sewing box) – China, 19th century***

436 These two objects are believed to be produced in China, therefore the use of *urushi*
437 lacquer (*qi* lacquer in Chinese) was expected.

438 In the case of object 49009, the pyrogram is dominated by the presence of aliphatic
439 carboxylic acids, including dicarboxylic acids (sebacic, azelaic and suberic acids) with
440 high relative abundance and a characteristic distribution indicative of the use of a drying

441 oil, possibly *tung* oil [23, 27, 45]. The pyrogram also enabled alpha-cedrene, beta-
442 cedrene and cedrol to be identified. These are the main components of the essential oil
443 from cedar, another known additive in lacquer formulations [27].

444 The extracted ion chromatograms of alkylbenzenes and alkylcatechols are in perfect
445 agreement with the chromatographic features of *urushi* (Figure 1, Table 2), therefore
446 pointing towards the authenticity of the object as being produced in China with
447 traditional materials used in lacquer preparation. Additionally, a series of compounds
448 referred to as alkylphenylcarboxylic acids was identified and these compounds form
449 when the drying oil is mixed with the lacquer [23, 24].

450 A very similar composition was found for object 48165, which was therefore also
451 confirmed as a traditional Chinese lacquered object.

452 In the case of object 49009, the surface was not shiny and this led us to consider its
453 study by FESEM-EDS. Observations of a micro-sample from this plate highlighted a
454 different way of decorating the surface compared to all the other samples. In fact, the
455 object is coated with a first layer of lacquer probably containing calcium carbonate (Ca,
456 C and O detected by EDS analysis). However, instead of a second sealing coating with
457 lacquer, a red pigmented lacquer layer is directly applied onto the ground (Figure 4d).

458 The decorative layer is 10-15 μm thick and is composed of vermilion with pigment
459 particles with 2-4 μm of total diameter. Finally, a thicker transparent finishing layer (15-
460 30 μm thick) is applied on the top of the coloured layer. The irregular thickness of the
461 layers and the lack of some expected layers seem to be the result of a decoration
462 process carried out with poor polishing and for an object of poor quality or value.

463

464 **4. CONCLUSIONS**

465 This study presents the results of an investigation carried out to assess the provenance
466 of a series of lacquered objects from the Museum of Zaragoza (Spain). The lacquer
467 identification was carried out based on the pyrolytic profiles and molecular markers
468 reported in the literature and following a decisional scheme which was implemented to
469 help the data analysis in order to distinguish the three Asian lacquers - *urushi*, laccol and
470 *thitsi*. In addition, some of the reported cases represent analytical situations, which are
471 often neglected in the literature. In particular, a possible mixture of *urushi* and *thitsi* is
472 discussed, as well as examples of *urushi* and *thitsi* identified after careful examination
473 despite the predominant presence of restoration materials.

474 The chemical information obtained by Py(HMDS)-GC/MS was coupled with the study of
475 the decoration techniques by FESEM-EDS. The study of the cross-sections added
476 significant information about the nature of the pigments (mercury sulphide, iron oxides,
477 gold powder, etc.) used to prepare the coloured layers and highlighted different ways of
478 applying the coating layers. Traditional techniques (*yun*, *maki-e*, *shitachi*, *shwe-zawa*,
479 *etc.*) were recognised and some chemical considerations were supported.

480 The overall results allowed us to confirm the geographical provenance of six out of the
481 eight objects investigated, whereas for two of them this information must be re-
482 evaluated. This confirms the robustness of Py(HMDS)-GC/MS as analytical technique to
483 characterise and distinguish Asian lacquers, as well as the importance of undertaking
484 scientific analysis to support historical and art historical information on museum
485 objects.

486

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495

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