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# Characterization and identification of an archaeological “lacquer” pipe

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## Abstract

A pipe with red coating on the surface was excavated from an archaeological site in Sweden, which is supposed to be a lacquer ware imported from China due to the admiration and pursue of lacquer wares from Asia by Europeans during sixteenth to eighteenth centuries. However, materials such as shellac and resins were often used to imitate lacquer during that time in Europe. To determine whether the pipe was Chinese lacquer ware or not, attenuated total reflection of fourier transform infrared spectroscopy (ATR-FTIR), thermally-assisted hydrolysis and methylation pyrolysis gas chromatography-mass spectrometry (THM-Py-GC/MS) were conducted. The detection of significant amount of aleuritic acid, laccijalaric acid, laccishelloic acid, shellolic acid and jalaric acid represents that shellac is the main material used for the pipe coating rather than Chinese lacquer. Long chain fatty alcohols were found in the sample, indicating that the shellac is un-dewaxed. In addition, pine resin and turpentine were also found as additives in the pipe coating. Furthermore, pigments in the coating were determined as cinnabar and carbon black by scanning electron microscopy with element energy dispersive spectroscopy (SEM-EDS) and Raman spectroscopy. The results could definitely support the conservation of the pipe, and also provide the evidence of the cultural exchange between Europe and Asia.

**Keywords** Shellac, Lacquer, Turpentine, Pine resin, THM-Py-GC/MS

## Introduction

Lacquerwares are special heritage objects in Asia. Normally lacquer wares were made of wood and coated with oriental lacquer, a viscous liquid collected from lacquer trees grown in East Asia. It is composed of water, glycoprotein, laccase, and a mixture of different catechols, respectively, from *Rhus vernicifera* (mainly grown in China, Japan and Korea), *Rhus succedanea* (mainly grown in Vietnam and Chinese Taiwan), and *Melanorrhoea usitate* (mainly grown in Burma and Thailand) [1].

The history of using lacquer dates back to the Neolithic period. The earliest lacquer ware was unearthed at the Kuahuqiao site in Zhejiang province of China, more than 8000 years ago [2]. A 7200-year-old lacquered comb was discovered in the Mibiki site, Ishikawa Japan [3]. A large number of lacquer objects were found in Warring States Period (475–221BC) archaeological sites in China. In our previous research, materials used for lacquer wares excavated from Chu tombs were identified as origin from the lacquer tree- *Rhus vernicifera* [4, 5]. According to the other researchers, the materials, structure and lacquering techniques are distinct in Han (221BC–220AD) [6–9], Song [10] and Qing [9, 11, 12] Dynasties (960–1912AD). The additives in lacquer were usually used to optimize the physical properties of lacquer film, such as drying oils were used to retard the rate of hardening and increase the luster and elasticity of lacquer film [7]. Proteins were often added to the ground layer of Asian lacquerwares, such

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as blood, animal glue, with the advantage of increasing the durability of ground layer and strengthening the lacquer structures [13, 14].

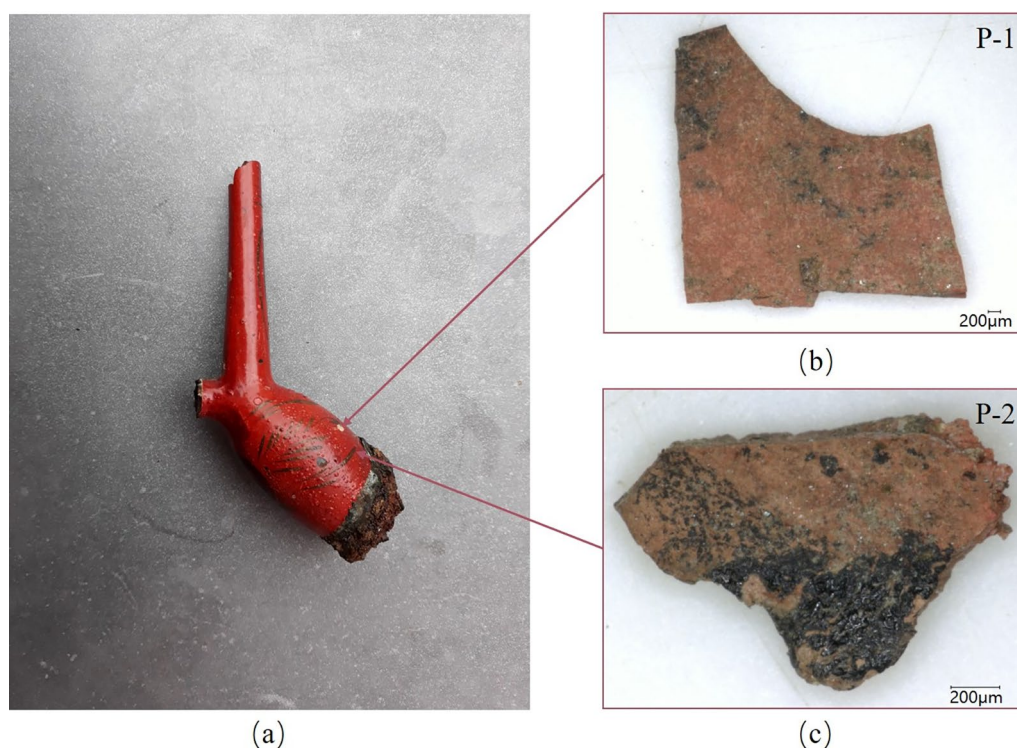
During the period of sixteenth to eighteenth centuries, lacquerwares from Asian were admired and pursued by Europeans, thus a number of lacquer objects were imported to Europe [15]. Due to the high cost of lacquer and limited production, European artisans tried to imitate Chinese lacquer with other plant resins and oils. As the study of lacquerware improved, artisans produced high-quality European lacquerware that became visually difficult to distinguish between European and Asian lacquerware. The recipes of Europe lacquer are extensive, the raw materials covering shellac, pine resin, turpentine, copal, benzoin and drying oil [16, 17].

Shellac is a natural resin mixture secreted by scale insects (*Kerria lacca* also known as *Laccifer lacca* Kerr or stick-lac) [18]. It consists of resin, dye, and wax [19, 20]. Normally, part of the water-soluble colorant and wax are removed through extraction process. Shellac resin is extracted by heating the *Kerria Lacca* in weak alkaline solution which has excellent film-forming and water-resistant properties. Shellac can form a smooth, durable film with good adhesion and is a non-toxic natural renewable resource. It was widely used as coating on furniture and other utilities [20, 21]. It was also known to

ancient Greek and Roman writers and used in Europe for furniture finishing during the late fifteenth century [22].

The main technique for Shellac resin analysis is gas chromatography mass spectrometry (GC/MS), by detecting the monomer composition, such as fatty acids and sesquiterpenic acids in shellac resin [23–26]. LC–MS method was also used for detection of shellac resin [8, 23]. Recently, the binding media used in Kezil paintings in China were identified as Shellac resin by pyrolysis-techniques for the study of lacquerwares gas chromatography/mass spectrometry (Py-GC/MS) analysis [27]. While the techniques for the study of lacquerwares include ELISA [2], Fourier Transform Infrared Spectroscopy (FTIR) [10, 11], Py-GC/MS [15, 27–29] and thermally assisted hydrolysis-methylation pyrolysis-gas chromatography/mass spectrometry (THM-Py-GC/MS) [4, 5, 30]. Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM–EDS) [6, 31] and Raman spectroscopy [9, 11] are normally applied to analyze the inorganic materials present in lacquer wares [8, 32].

In the present work, a wooden pipe with red coating on the surface from an archaeological site (dates back to seventeenth century) in Sweden (Fig. 1a) was studied to identify the materials used. The pipe looks like typical Chinese lacquer ware, with black bamboo patterns on the red surface of the object [29]. Tiny samples from



**Fig. 1** **a** The lacquer pipe from the Archaeological excavation site; **b** red fragment (labeled as P-1); **c** black fragment (labeled as P-2)

the coating of the pipe have been collected in order to obtain the information of inorganic and organic materials applied in the coating (Fig. 1 b, c). Initially, FTIR was used for the identification of the materials in the lacquer film. Secondly, THM-Py-GC/MS was applied for the identification of lacquer/resin and organic additives, since THM-Py-GC/MS technique has the advantage of analyzing multi-organic materials in a single sample analysis [5, 30]. Meanwhile scanning electron microscopy with element energy dispersive X-ray spectroscopy (SEM–EDS) and Raman microscopy were used for the pigment characterization.

## Materials and methods

### Materials

In order to investigate the coating materials in the lacquer pipe, two paint samples from the red and black areas (labeled as P-1, P-2) were taken, for the characterization of the pigments and the binding media (about 1–2 mg). Two examples of the studied objects are shown in Fig. 1.

Reference material of shellac (made in India) was purchased from a binding media shop in Beijing.

### Instruments and parameters

For ultra-depth three-dimensional (3D) video Microscopy analysis, an instrument made by Keyence, Japan (VHX-6000) was used. The lens was VH-ZST, and the magnification was 20–2000.

For scanning electron microscopy with element energy dispersive X-ray spectroscopy analysis (SEM–EDS), backscattered electron images (BSE) and elements of the samples were obtained by a Tescan Vega 3 XMU scanning electron microscope (SEM, Czech Republic) equipped with an EDS detector of Bruker Nano GmbH 610 M (Germany). The working distance is 15 mm and electro-beam intensity is 20 kV.

For Raman spectroscopy analysis, an instrument made by HORIBA Jobin Yvon S.A.S (LabRAMHR Evolution) was used. Black pigments and red pigments were studied using 632 and 786 nm laser excitation lines. The objective lens was 50 $\times$ , and the spatial resolution was 1–2  $\mu$ m.

For fourier transform infrared spectroscopy analysis (FTIR), data were obtained by a Nicolet iS5 Fourier transform infrared spectrometer (Thermo Scientific Corporation). The experiment set the acquisition mode to attenuated total reflection (ATR). The crystal used in the ATR attachment is diamond. The spectral resolution is 4  $\text{cm}^{-1}$  and the number of scans is 64 [47]. Each sample was scanned at 25  $^{\circ}\text{C}$  (room temperature) and the data acquisition system used was OMNIC. A spectral range of 4000–500  $\text{cm}^{-1}$  was selected for all samples.

A multi shot pyrolyser type PY 3030 D of Frontier Lab and a gas chromatograph mass spectrometer, GC/MS QP

2010 Plus of Shimadzu (Kyoto Japan) were employed. The pyrolysis was performed at 550 $^{\circ}\text{C}$  for 12 s. The pyrolyser interface was set at 290 $^{\circ}\text{C}$ .

A capillary column DB-5MS UI with a 0.18 mm internal diameter, 0.18  $\mu$ m film thickness and 20 m length [Agilent J&W] was used. The temperature of the oven was programmed from 35 $^{\circ}\text{C}$  (1.5 min) to 100 $^{\circ}\text{C}$  at 60 $^{\circ}\text{C min}^{-1}$ , and to 240 $^{\circ}\text{C}$  at 14 $^{\circ}\text{C min}^{-1}$ . Then the temperature was set up to 315 $^{\circ}\text{C}$  at 6 $^{\circ}\text{C/min}$ , which was held for 1.5 min. Column flow was set at 0.92 ml/min, and in split mode was set at 1:20 ratio. The temperature of the Ion source and the interface were 200 $^{\circ}\text{C}$  and 250 $^{\circ}\text{C}$ , scan from 35 to 500 m/z. The carrier gas was helium with an inlet pressure of 145.3 kPa.

## Results and discussion

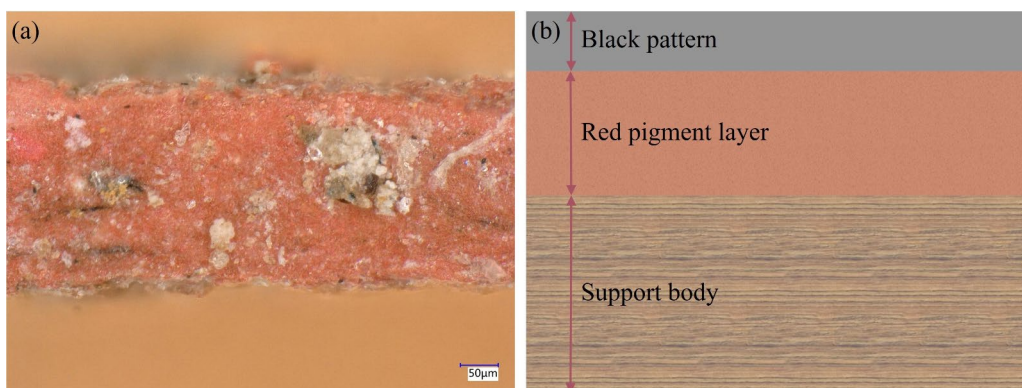
### The structure of the red coating of the lacquer pipe

The structure of the film was obtained by 3D video Microscopy analysis observing the cross-section of the samples. The image of the cross-section of samples was presented to depict coating layers (Fig. 2a): The black bamboo leaves pattern was on the surface of the red coating (Fig. 1a), which are about 60  $\mu$ m and 240  $\mu$ m thick, respectively, without ground layer. The schematic diagram is shown in Fig. 2b.

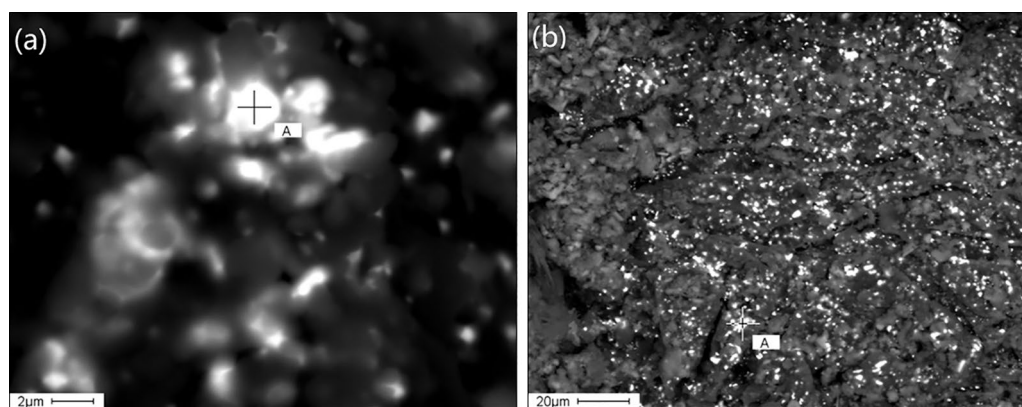
The pigments in the coating layer were analyzed by SEM–EDS and Raman spectroscopy. The images in Fig. 3a, b depicted the morphology of the red and black pigments from the sample P-1 and P-2. The pigment grains in the paint could be analyzed individually by EDS point analysis, as marked in the images. Raman spectra of the red and black pigments are shown in Fig. 4. The results obtained by EDS analyses were list in Table 1. The red pigment could be identified as the cinnabar (HgS) by the high content of mercury and sulphur, as well as the Raman peaks at 251,341  $\text{cm}^{-1}$  [33]. For the black pigment, the Raman spectrum showed two broad bands at 1363 and 1606  $\text{cm}^{-1}$ , which indicates the presence of carbon-based black [34]. The carbon-based black pigment used in works of art is also mentioned in the published literature on the illustrations of manuscripts [35] and wall paintings [36, 37].

### ATR-FTIR analysis of the pipe coating and shellac

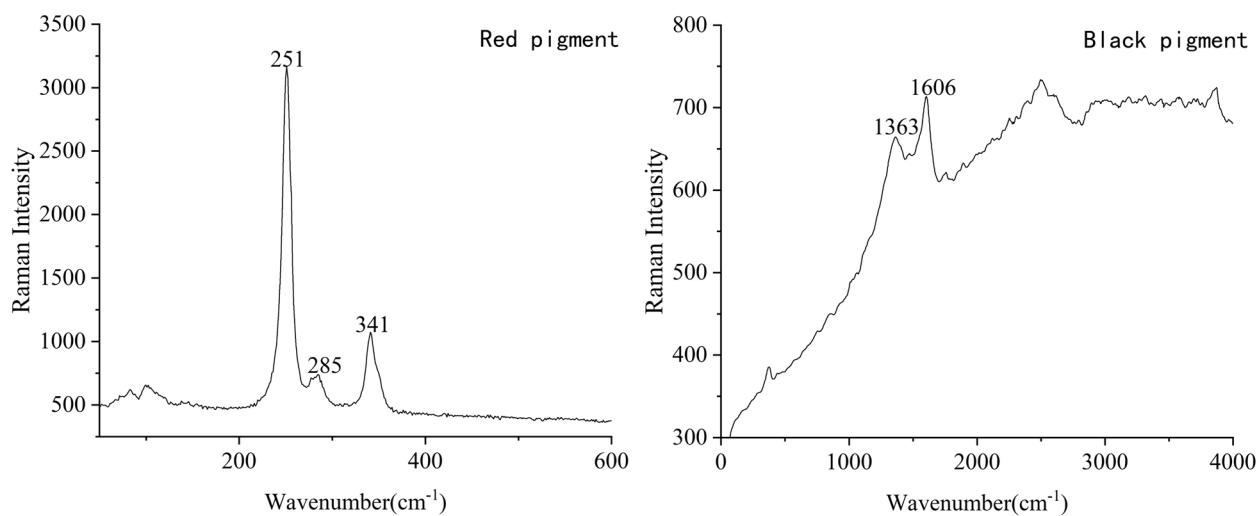
The binding media of the pipe coating materials were initially analyzed by ATR-FTIR. The FTIR spectra of sample P-1 is shown in Fig. 5a. The sample has a broad absorption peak near 3440  $\text{cm}^{-1}$ , which is the symmetric stretching vibration peak of –OH. The two small peaks of 3740 and 3850  $\text{cm}^{-1}$  were found in the archaeological sample, also deriving from hydroxyl groups. They are not a common one in organics, but may be assigned to some minerals containing water. Two sharp peaks at 2931  $\text{cm}^{-1}$



**Fig. 2** a Micrographs of the sample P-1; b a schematic diagram of the coating of the pipe



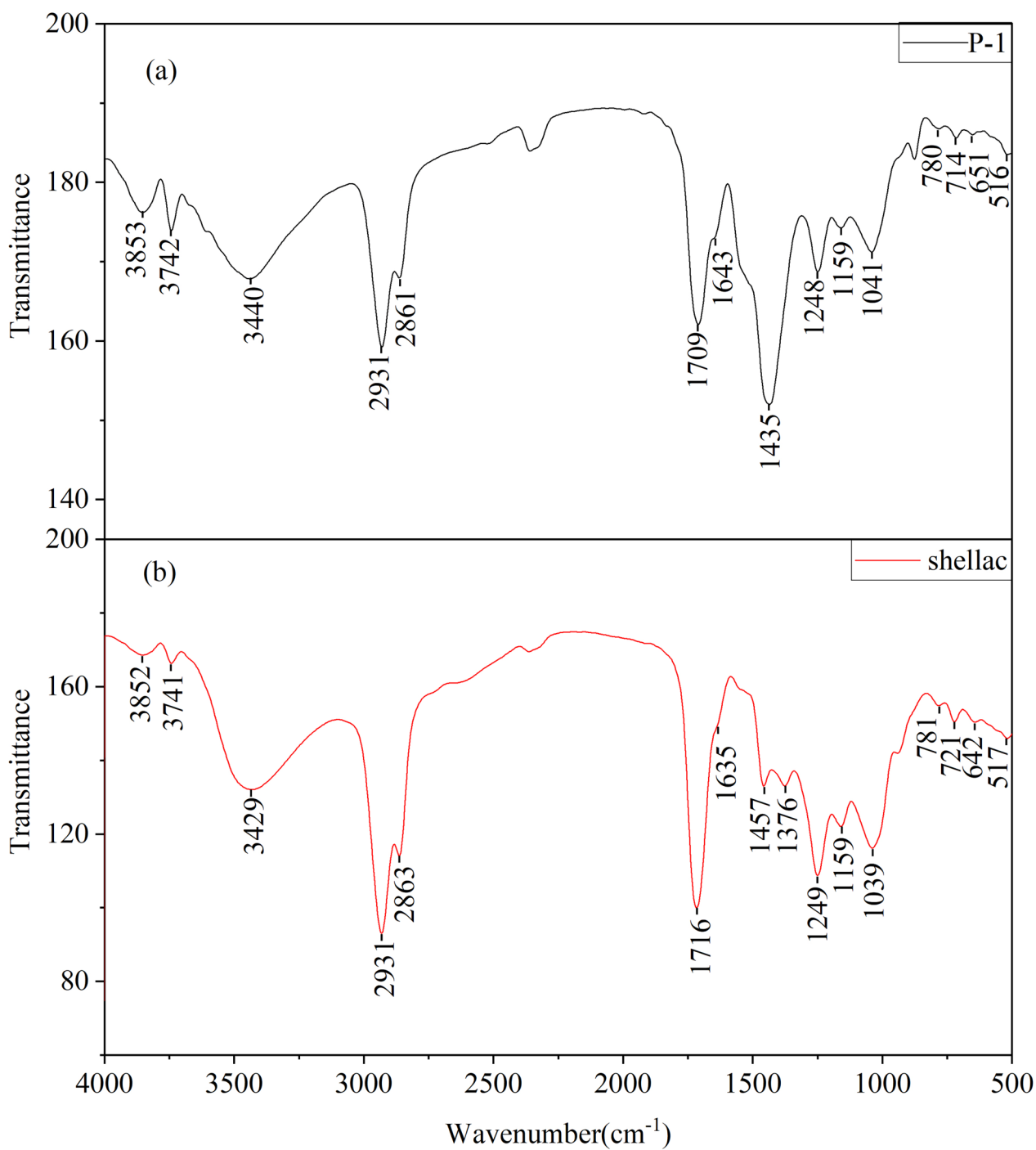
**Fig. 3** SEM-micrograph of the samples: a P-1; b P-2; the marked particles in the images (a–b) were analyzed individually by EDS point analysis, as shown in Table 1



**Fig. 4** Raman spectra of red and black pigment (sample P-1, P-2)

**Table 1** List of samples from the coating of the pipe and the results obtained by SEM/EDS (at/%)

Spot	Element									
	Na	Mg	Al	Si	P	S	K	Ca	Fe	Hg
P-1-A	-	-	4.82	16.12	4.78	36.01	-	22.24	-	16.02
P-2-A	1.87	3.57	9.25	28.05	7.90	18.72	3.15	16.61	3.18	7.70



**Fig. 5** ATR-FTIR spectra of **a** sample P-1 and **b** shellac

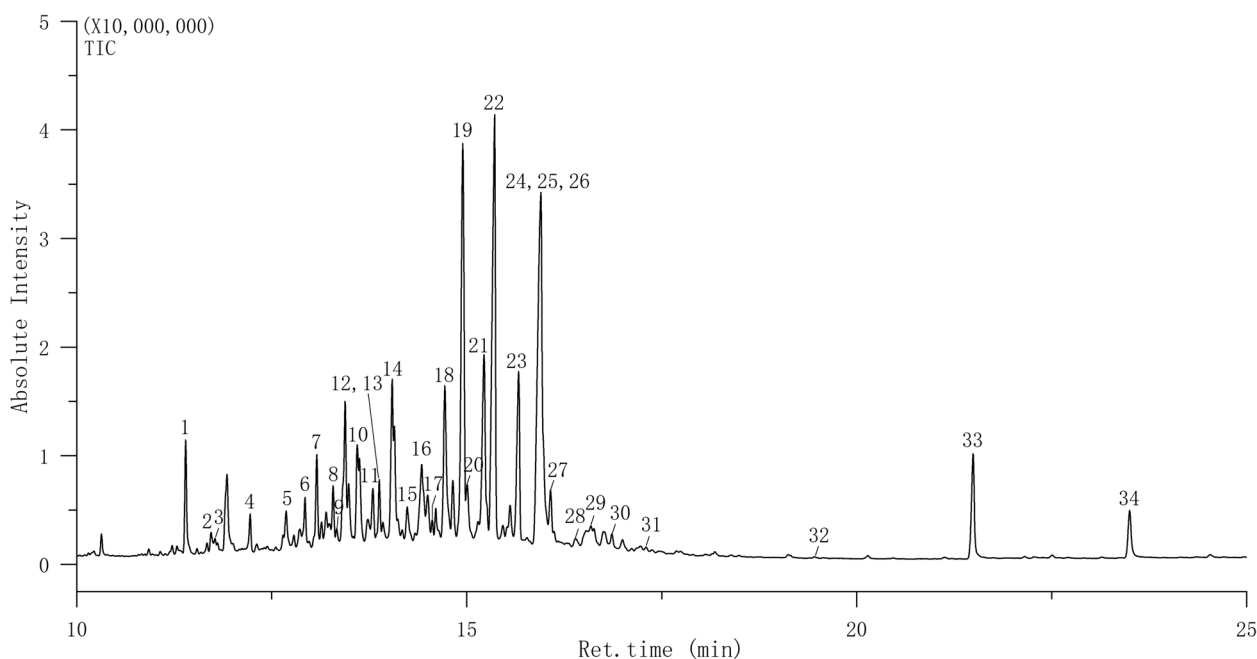
and near  $2863\text{ cm}^{-1}$  were ascribable to C–H stretching. The prominent peak at  $1709\text{ cm}^{-1}$  was due to C=O stretching in carboxy group, which is distinguishing band of resins [38]. The band at  $1435\text{ cm}^{-1}$  was indicative of  $-\text{CH}_2-$  and  $-\text{CH}_3$  asymmetric bending or deformation,  $1376\text{ cm}^{-1}$  of  $-\text{CH}_3$  symmetric deformation, 1248 and  $1159\text{ cm}^{-1}$  of O–H bending and C–O stretching overlapping C–O stretching from ester group [40]. The peak at  $1041\text{ cm}^{-1}$  gives information about C–O stretching of ether or acetal groups. The band at  $714\text{ cm}^{-1}$  reveals the C–H [40]. In agree with the literature [38], one band between  $1650\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  and other band between  $1260\text{ cm}^{-1}$  and  $1238\text{ cm}^{-1}$  are characteristic for resin, not present in wax, carbohydrates and oils. The peak at  $1248\text{ cm}^{-1}$  in the sample gives a clue that resin might be present. In addition, there is an absorption peak at  $1622\text{ cm}^{-1}$  of benzene ring in the infrared spectrum of lacquer [39], which is not detective in the ancient sample. Therefore, it seems that the pipe coating is more like resin than lacquer. Possibly, the pipe was coated with European imitation lacquer that bore resemblance to Asian lacquer. Shellac is a main material commonly used in European lacquer, which is a natural resin secreted by lac insect from Southeast Asia. The same FTIR procedure was subsequently applied to the reference sample of shellac, the spectra obtained is shown in Fig. 5b. It is obvious that the sample P-1 have similar spectral peaks to shellac, especially the fingerprint region at  $1500\text{--}600\text{ cm}^{-1}$ , indicating that the pipe coating may contain shellac. In

order to further clarify the composition of the pipe coating, THM-Py-GC/MS analysis was conducted.

#### Study the coating film from the pipe sample by THM-Py-GC/MS

The pipe sample was analyzed by THM-Py-GC/MS. The chromatogram obtained THM-Py-GC/MS is depicted in Fig. 6, as well as the identified compounds are listed in Table 2.

Aleuritic acid methyl ester, trimethyl ether (#22,  $m/z$  95) is the main peak, detected by pyrolysis and used as the diagnostic peak for shellac. A series of hydroxyl fatty acids were detected, including aleuritic acid, trimethyl isomers (#24,  $m/z$  95), aleuritic acid, methyl ester, 10,16-dimethyl ether (#25,  $m/z$  95) and aleuritic acid, methyl ester, 9,16-dimethyl ether (#26,  $m/z$  45). The corresponding mass spectra were listed in Additional File 1: Fig. S1. The identification of aleuritic acid, trimethyl isomers due to isomerization of polyunsaturated fatty acids in the presence of TMAH [25]. For improving the sensitivity of target analysis, differentiation between ingredients with similar retention times on the basis of chromatographic data could be accomplished by the deconvolution algorithm of the Automatic Mass Spectral Deconvolution and Identification System (AMDIS) except extracted ion technique. It was evident that aleuritic acid, trimethyl isomers, aleuritic acid, methyl ester, 10, 16-dimethyl ether and aleuritic acid, methyl ester, 9, 16-dimethyl ether were extracted



**Fig. 6** TIC of the sample P-2 obtained by THM-Py-GC/MS analysis

**Table 2** The compounds identified in the sample P-2 by THM-Py-GC/MS (the bold values are characteristic ions of the marker compounds)

Peak no	RT (min)	Area%	Marker compounds of pine resin	Main ions
1	11.40	1.90	Butolic acid,6-methoxy, methyl ester	55,69,83, <b>127</b> ,159
2	11.72	0.54	Butolic acid lactone	41, <b>55</b> ,67,85,113
3	11.77	0.33	Butolic acid, methyl ester	55,67, <b>87</b> ,113,145
4	12.22	0.94	9,10-Dimethoxytetradecanoic acid, methyl ester	45,69, <b>101</b> ,137,201
5	12.69	1.08	Laccijalaric acid, trimethyl, isomer 1	75,151, <b>274</b> ,306
6	12.93	0.4	Laccijalaric acid, trimethyl, isomer2	75,151, <b>274</b> ,306
7	13.08	1.18	Epimanool	69,81,95, <b>137</b> ,107
8	13.29	1.15	Laccishelloic acid: dimethyl ester, methyl ether	87,167, <b>262</b> ,275,307
9	13.33	0.61	Turpentine aged pyro product	105, <b>119</b> ,131,185,255
10	13.60	1.91	9,10-Dimethoxyhexadecanoic acid, methyl ester	55,97,129,137, <b>201</b>
11	13.80	1.33	Shellac, unverified 1	131,145,159,187, <b>247</b>
12	13.88	0.73	Shellac, unverified 2	131,145,159,187, <b>247</b>
13	13.88	0.55	Jalaric acid, tetramethyl	75,91,272, <b>291</b> ,304
14	14.04	3.25	Larixol-methoxy	41,69,95,107, <b>167</b>
15	14.24	1.61	Shellolic acid: dimethyl ester, dimethyl ether	85,95,162,238, <b>320</b>
16	14.42	3.02	Methyl pimarate	91, <b>121</b> ,180,257,316
17	14.56	0.66	Methyl sandaracopimarate	91,105, <b>121</b> ,301,316
18	14.72	4.34	Larixol	43,55, <b>69</b> ,95,109
19	14.90	0.16	Jalaric acid, trimethyl	75,91,272, <b>291</b> ,304
20	14.95	8.97	Methyl isopimarate	41,67,81, <b>241</b> ,257
21	15.22	5.11	Methyl dehydroabietate	43,141, <b>239</b> ,299,314
22	15.36	10.39	Aleuritic acid methyl ester, trimethyl ether	71, <b>95</b> ,137,159,201
23	15.67	4.28	Methyl abietate	121,213,241, <b>256</b> ,316
24	15.95	13.09	Aleuritic acid, trimethyl isomers	71, <b>95</b> ,137,145,201
25	15.95	11.64	Aleuritic acid, methyl ester, 10,16-dimethyl ether	45,71, <b>95</b> ,155,187
26	15.95	11.56	Aleuritic acid, methyl ester, 9,16-dimethyl ether	<b>45</b> ,55,137,145,201
27	16.07	1.39	Methyl neoabietate	91,121, <b>135</b> ,148,316
28	16.40	0.85	Methyl 12-methoxyabieta-8,11,13-trien-20-oate	227,255, <b>269</b> ,329,344
29	16.59	0.82	15-Methoxydehydroabietic acid, methyl ester	43,73,269,313, <b>329</b>
30	16.86	0.92	15-Hydroxydehydroabietic acid, methyl ester	43,59,255, <b>315</b> ,330
31	17.30	0.35	7-Oxodehydroabietic acid, methyl ester	187,213, <b>253</b> ,269,328
32	19.46	0.09	1-Hexacosanol, methyl ether	43,57,69, <b>83</b> ,97
33	21.49	2.85	1-Octacosanol, methyl ether	43,57,69, <b>83</b> ,97
34	23.50	1.46	1-Triacontanol,methyl ether	43,57,69, <b>83</b> ,97

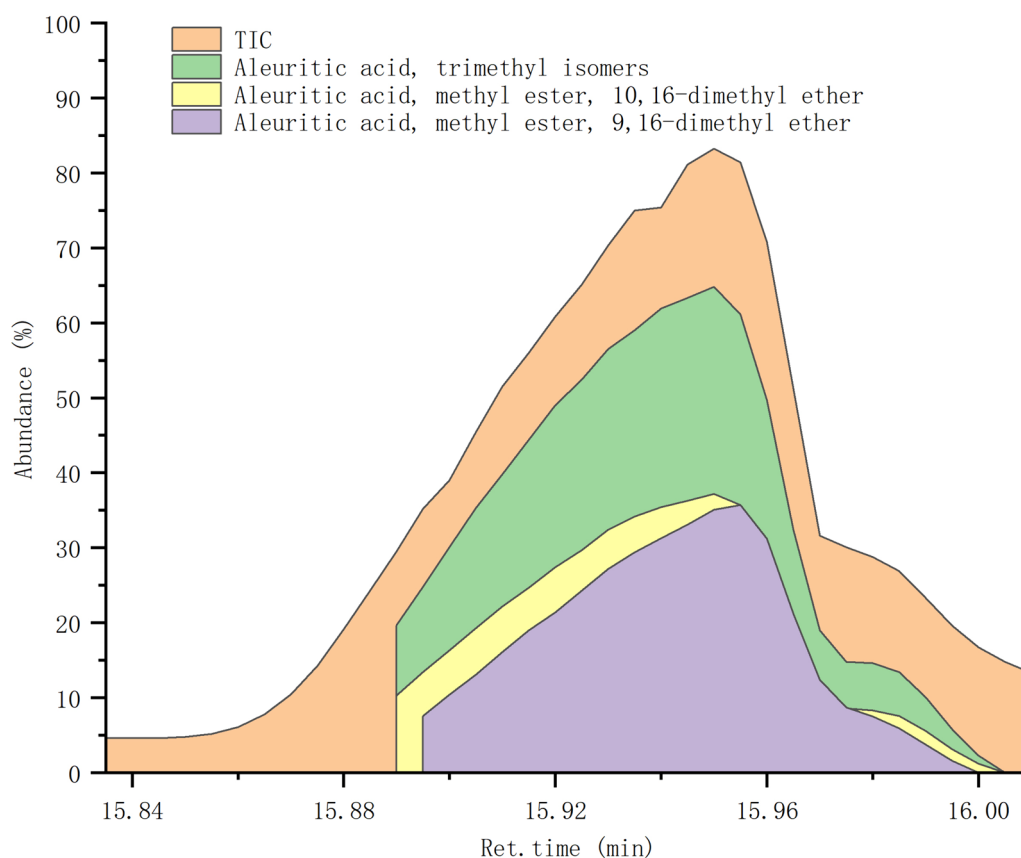
after the deconvolution of the components, shown in Fig. 7 and the corresponding mass spectrum in supplementary materials.

The identification and characterization of several methyl derivatives of cyclic terpene acids evidenced another category of representative components of lac resin, which were laccijalaric acid (#5, #6), laccishelloic acid (#8), shellolic acid (#15) and jalaric acid (#13, #19), respectively. Laccishelloic (#8, m/z 262) and shellolic acid (#15, m/z 320) were formed by Jalaric and laccijalaric acid through Cannizzaro-type disproportion

reaction in the presence of TMAH, which were are consistent with previous literature [25, 26, 42, 43].

Apart from polyhydroxy fatty acids and sesquiterpene acids, 9,10-dimethoxytetradecanoic acid, methyl ester (#4, m/z 101) and 9,10-dimethoxyhexadecanoic acid, methyl ester (#10, m/z 201) as minor acids of shellac were detected in accordance with the literature [44].

Additionally, the derivatives of butolic acid with TMAH (#1, #2, #3, the corresponding mass spectra were listed in Additional file 1: Figure S2) are also the typical pyrolysis products of shellac. However,



**Fig. 7** Aleuritic acid derivatives of the pipe sample extracted from a single TIC peak

these compounds cannot always be detected, probably depending on the source of lac [25] or the pyrolysis conditions.

Long-chain alcohol derivatives using TMAH as methylation reagent (Additional File 1: Fig. S1) including 1-hexacosanol, methyl ether (#32,  $m/z$  83), 1-octacosanol, methyl ether (#33,  $m/z$  83) and 1-triacontanol, methyl ether (#34,  $m/z$  83) were found in the sample. Although long-chain alcohols are generally considered as the marker compounds of beeswax, they can be also detected in wax-containing shellac [45]. There were only a few long-chain alcohols identified in the sample, essentially 1-Octacosanol, methyl ether, which is not consistent with beeswax and other wax, indicating that they were more likely originated from shellac which have not been dewaxed [46, 47].

The chemical compounds derived from pine resin, including methyl pimarate (#16,  $m/z$  121), methyl isopimarate (#20,  $m/z$  241), methyl abietate (#23,  $m/z$  256) and methyl neoabietate (#27,  $m/z$  135) were found in the sample. Furthermore, the oxidization products of

pine resin including methyl dehydroabietate (#21,  $m/z$  239), 7-oxo-dehydroabietic acid, methyl ester (#31,  $m/z$  328) and 15-methoxy/hydroxydehydroabietic acid, methyl ester (#29:  $m/z$  329/#30:  $m/z$  315) were also detected, representing the presence of pine resin in the sample. Pine resin was frequently used to improve the physical and chemical properties of the shellac coating [41]. In the field of cultural relics, apart from pine resin, other materials such as lacquer, drying oils were mixed with shellac to make adhesives and coatings [15, 46, 48, 49].

Epimanol (#7,  $m/z$  137) and larixol (#18,  $m/z$  69) are marker compounds of turpentine [50–52]. Both turpentine and pine resin are extracted from conifer subfamily Pinaceae trees. Different from pine resin, turpentine has characteristic diterpenoid labdanes, mainly epimanol, larixol and larixol acetate. Moreover, turpentine aged pyrolysis product (#9,  $m/z$  119) and Larixol-methoxy (#14,  $m/z$  167) also belong to pyrolyzates of turpentine [53]. Turpentine was commonly used as



an additive in art paintings to modify the properties of the paint film [54, 55].

Upon THM-Py-GC/MS analyses, three groups of compounds were identified, which originated from shellac, pine resin and turpentine, respectively, demonstrating the organic materials used to make the coating of the pipe.

## Discussion and conclusion

In order to identify the materials used in the archaeological pipe from Sweden, scientific analyses were carried out, including SEM–EDX, Raman spectrometry, ATR-FTIR and Py-GC/MS analyses. Shellac, pine resin and turpentine were identified as the coating materials of the pipe while cinnabar and carbon black as colorants.

According to the scientific results, the amount of shellac in the pipe coating was obviously higher than those of pine resin and turpentine, which indicates that shellac was utilized as the main material and the other two was used as additives. Since the sixteenth century, Chinese lacquerware has been welcomed in the European market. As the high demand for Chinese lacquerware could not be satisfied, Europeans began to prepare alternative imitation varnish. The invention of shellac varnish is closely related to the excellent film-forming property, low permeability and good adhesion of shellac [56]. According to the literature [16], the addition of pine resin in shellac can soften and add flexibility to the coating, and other materials, including camphor, elemi, and essential oils were occasionally added to significantly slow the drying of the film. The composition of shellac, pine resin and turpentine is one of classical recipes of Europe lacquer. The results can not only support the conservation and restoration of the pipe, but also provide a evidence of cultural exchange between Europe and southeast Asia.

The findings of scientific analysis can offer insights for the conservation of the pipe. Such as, unlike lacquer, organic solvents should be absolutely avoided since shellac dissolves in common solvents like ethanol and ethers. Additionally, heat would lead to softening and melting.

The origin of the pipe is an interesting topic due to the detection of shellac. Except material technical aspects, when it comes to determining the use of shellac in Europe lacquer, availability of it plays an important role. Lac insect inhabits on trees of various species in tropical regions of Asia, primarily China, India, Thailand, Vietnam, and Myanmar, making shellac a local product of the above areas. During sixteen-eighteenth century, shellac was commonly transported in large quantities to Europe from India, which was used to paint on furnishings in Europe to imitate lacquerware from China and Japan, especially with the establishment of commercial companies [57]. However, the origin of the pipe was still

doubtful as far. It might be made in south east Asia and sold to Europe or produced in Europe using the shellac sourced from southeast Asia. Still, it is evidence that culture exchange between Europe and Asia.

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-024-01256-8>.

**Additional File 1:** The mass spectra of aleritic acid derivatives and butolic acid derivatives. **Fig. S1** Mass spectra of Aleritic acid derivatives. (a Aleuritic acid methyl ester, trimethyl ether; b aleuritic acid, trimethyl isomers; c. aleuritic acid, methyl ester, 10, 16-dimethyl ether; d aleuritic acid, methyl ester, 9,16-dimethyl ether). **Fig. S2** Mass spectra of butolic acid derivatives. (aButolic acid,6-methoxy, methyl ester; b butolic acid lactone; c butolic acid, methyl ester).

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## Author contributions

YH completed the experiments on Raman, ATR-FTIR, THM-Py-GC/MS, data analysis and draft of the article, DWS carried out microscope and SEM-EDS analysis, YF revised the experimental details, KL involved in archaeological excavation and provided the sample information. the SW provided the guidance on experiments and conceived the outline of the paper. All authors participated in the discussion and conclusion of the paper.

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## Availability of data and materials

Not applicable.

## Declarations

### Ethics approval and consent to participate

Not applicable.

### Competing interests

The authors declare no competing interests.

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