Journal of Cultural Heritage 62 (2023) 13–20

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

Original article

Temporary solidification and extraction of marine archaeological wood underwater at a depth of seven meters: A further contribution

Xinxin Wang[a], Hao Wang[b], Bingjian Zhang[a,c,*], Yulan Hu[a], Longguan Zhu[c]

[a] Department of Cultural Heritage and Museology, Zhejiang University, Hangzhou 310028, PR China
[b] National Centre for Archaeology, Beijing 100013, PR China
[c] Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 15 September 2022
Accepted 5 May 2023

Keywords:
Underwater archaeology
Cultural relics
Temporary solidification
In-situ solidifying
Veratraldehyde

ABSTRACT

In-situ solidifying extraction of large-volume and severely damaged underwater fragile artifacts is still one of the major issues in underwater archaeology. Recent evidence suggests that veratraldehyde can be used to temporarily solidify artifacts underwater; however, it is still challenging to use it in actual archaeological sites. This prospective study was conducted in a seven-meter-deep pool wherein veratraldehyde was used to solidify and extract waterlogged ship wood from the "Nanhai I" shipwreck. The entire underwater extraction process was recorded using a camera. The change in the wood surface color before and after extraction was relatively minor. Scanning electron microscopy analysis revealed that the wood microstructure was not significantly damaged, while nuclear magnetic resonance analysis showed no residues of veratraldehyde and its oxidation products. Overall, the proposed method utilizes a set of scientific techniques for successful in-situ solidifying extraction of underwater fragile wooden artifacts.
© 2023 Consiglio Nazionale delle Ricerche (CNR). Published by Elsevier Masson SAS. All rights reserved.

1. Introduction and research aim

Underwater archaeology is an extension of land archaeology, encompassing the study of shipwrecks as well as submerged sites such as lakes, wells, and reservoirs [1]. Since the majority of the oxygen content is isolated underwater, artifacts including bamboo and wood wares, porcelain, and iron wares remain intact for a long time [2]; however, the underwater environment is complex and may comprise various acids, alkalis, salts, and microorganisms, which can damage organic artifacts [3]. United Nations Educational, Scientific and Cultural Organization (UNESCO) clearly stated in 2001 that underwater heritage should be primarily preserved via in-situ conservation [4]; however, certain fragile organic artifacts can be damaged via continuous in-situ conservation and even lose key information contained in them [5–7]. Thus, it is necessary to design a set of extraction methods for underwater fragile artifacts.

At present, two attempts have been made to extract underwater artifacts: (1) "overall extraction" represented by the salvage of the "Nanhai I" shipwreck through a steel caisson in 2007, which was placed in the museum for future excavation and protection experiments [8]; (2) "in-situ solidifying extraction", which involved carbon fiber-epoxy and liquid nitrogen reinforcement, as proposed by the Danish National Museum in 2014 [9]. Since the former approach requires a lot of human and financial resources, it cannot be used to extract small artifacts; the latter method provides a better preservation of the composition and relative position of the artifacts, which is crucial for extracting key information. However, the current way inevitably needs to turn over the artifacts and therefore cannot be classified as strictly in-situ solidifying extraction. To improve the underwater in-situ solidifying extraction method, researchers have begun to consider the possibility of using a temporary solidifying method for underwater archaeology applications [4,10,11].

Studies over the past three decades have provided important information regarding temporary solidifying materials used in inland archaeological excavations. Because the materials used can undergo rapid solidification and easily vaporize, in-situ solidifying extraction of fragile artifacts are reversible processes that will not damage the artifacts. Surveys such as those conducted by Rowe [12] have shown that cyclododecane has since proved to be a versatile and useful material, which has been used to conserve several materials, including wall paintings, plaster, ceramics, paper, textiles, and metals [13]. Its ability to sublime without residues

* Corresponding author at: Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China.
E-mail address: zhangbiji@zju.edu.cn (B. Zhang).

https://doi.org/10.1016/j.culher.2023.05.012
1296-2074/© 2023 Consiglio Nazionale delle Ricerche (CNR). Published by Elsevier Masson SAS. All rights reserved.

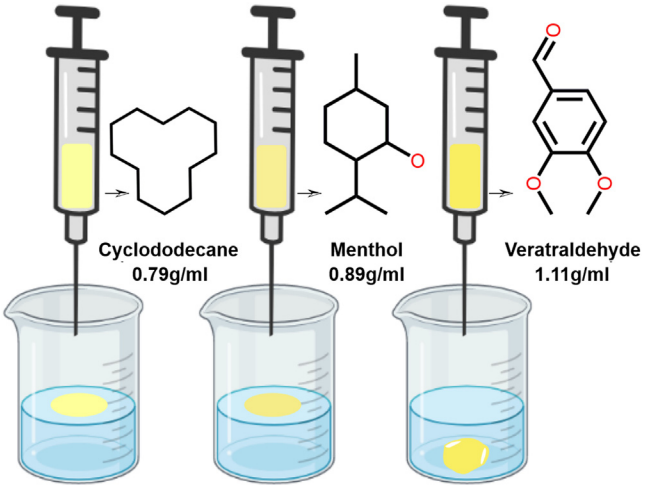

Fig. 1. Comparison of the performance underwater of cyclododecane, menthol, and veratraldehyde.

is particularly exciting for conservators since it can function as a temporary consolidant, binding medium, adhesive, or support material that is fully recyclable [14,15]. Han et al. found that menthol is more user-friendly and successfully used it to conduct extraction at the excavation site (Pit 1) of the mausoleum of the First Qin Emperor [16,17]. Although these two compounds have played a significant role in artifact conservation and proven their safety through the test of time, they are less dense than water and cannot undergo phase change underwater from liquid to solid, as shown in Fig. 1.

Researchers have tested several materials and found that veratraldehyde meets the requirements for temporary solidification [18]; consequently, it has been used to extract submerged clay pots and lacquer trays in the laboratory successfully [19]. Several parameters, including salinity, hydrostatic pressure, and water temperature, were also found to affect the solidifying rate of veratraldehyde [20]. However, the abovementioned studies were carried out in laboratories that cannot replicate actual conditions. In this study, the extraction experiment of waterlogged ship woods from the “Nanhai I” was conducted in a seven-meter-deep pool by archaeological divers who tested the feasibility of this method underwater. The entire extraction process was recorded using an underwater camera for providing a practical demonstration of temporary solidification and extraction.

2. Materials

Four pieces of waterlogged wood from the "Nanhai I" shipwreck (K4NH-3), numbered W1–W4, were selected for this study. The species of the wood were cedar (*Cunninghamia lanceolata*) and masson pine (*Pinus massoniana.*), as shown in Fig. 2. The ship woods are highly decayed with a moisture content over 500%; W1 measures 20.5 cm long, 9.6 cm wide on the left, 5.0 cm wide on the right, and 3.2 cm thick; W2 measures 45.4 cm long, 5.0 cm wide on the left, 3.8 cm wide on the right and 0.8 cm thick, with some lacquer residue in the upper left corner; W3 measures 14.6 cm long, 3.8 cm wide and 1.2 cm thick; W4 measures 13.5 cm long, 4.2 cm wide and 1.6 cm thick. Due to their fragility, the ship woods must be handled carefully during extraction. The remaining lacquer can be tested for ethanol dissolution to assess safety [21] i.e., determine whether the ethanol solution will dissolve the lacquer on the wood.

Veratraldehyde (Maclin) used in this study exhibited a melting point of 40–43 °C, density of 1.114 g/mL (at 25 °C), water solubility of <0.1 g/100 mL (at 22 °C), and acute toxicity (orally fed to rats and showed a medium lethal dose (LD_{50}) of 2000 mg/kg; <25 is highly toxic, 25–200 is toxic, 200–2000 is harmful).Furthermore, an electronic analytical balance, a constant temperature water bath, a freeze dryer, a scanning electron microscope (SEM, SU8000), and a nuclear magnetic resonance spectrometer (^{1}H-NMR600Hz, Agilent DD2 600) were used.

3. Methods

3.1. Procedures

The following procedures were employed in this study: making insulating bottles, placing fragile ship woods underwater, developing a shape-shifting metal fence, sampling, and color analysis. The insulating bottles shown in Fig. 3 were used to prepare molten veratraldehyde, which does not solidify during the extraction. Its outer layer is made of a hard polypropylene (PP) film, inner layer is composed of polyethylene terephthalate (PET), and middle layer is made of rare-earth silicate that provides better insulation and sealing. Consequently, filling the bottle with molten veratraldehyde, we heat-sealed the aluminum foil to further enhance the seal. With

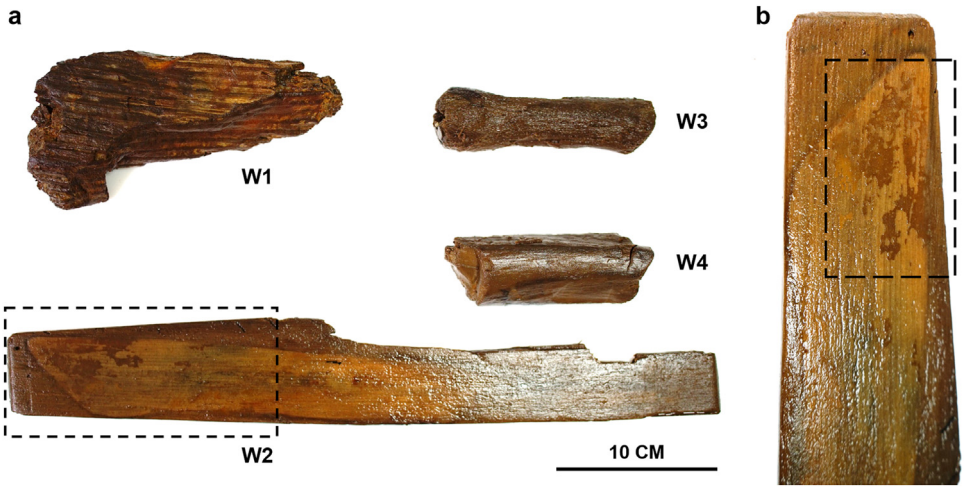

Fig. 2. (a) Images of W1–W4 samples from the “Nanhai I” shipwreck, (b) enlarged view of the W2 sample surface comprising lacquer residue.

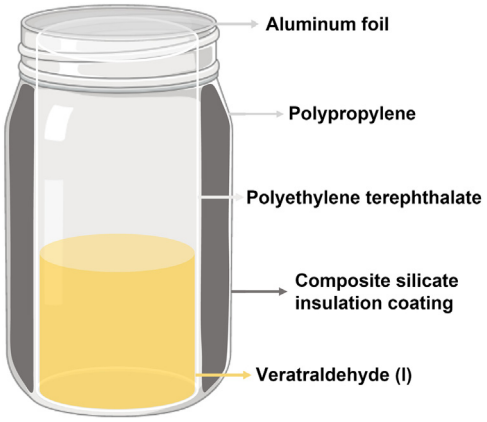

Fig. 3. Structural diagram of the insulating bottle.

these measures, the insulated bottle can withstand depths of up to 10 m underwater for at least an hour without deformation, and the veratraldehyde does not crystallize.

The fragile ship wood samples (W1–W4) were placed in underwater sand at random (Fig. 5a).

Based on the artifact form underwater, a 100-mesh sieve made of 304 stainless steel was used to fabricate a shape-shifting piece that can enclose an area, thereby preventing the exudation of molten veratraldehyde and solidifying the fragile artifacts inside the enclosed area. We determined the ductility and porosity in our previous study [20] and coated the surface with microcrystal wax to better prevent veratraldehyde exudation.

A color difference analysis was conducted to ascertain whether using veratraldehyde can change the color of the ship wood surface. Consequently, a colorimeter was used to quantify the colors of W1 and W4 samples before and after the extraction, with at least three measurements points being used per sample and three tests being conducted per point.

3.2. Extraction process underwater

Veratraldehyde was melted in a 60 °C hot water bath, injected into the insulating bottles and exhausted air, and sealed with aluminum foil via hot pressing. Archaeological divers delved into the bottom of the seven-meter-deep pool, and placed the shape-shifting metal mesh onto the sand surrounding the ship wreck at a depth of 1–3 cm. The sand on the ship wood was gently cleaned with a polypropylene fiber cloth to ensure the bonding of veratraldehyde and wood, thus enhancing the mechanical strength of the solidification. Molten veratraldehyde was slowly poured in stages until the liquid level became higher than the fiber cloth by 1–2 cm. After veratraldehyde was solidified, the procedure was repeated until the metal mesh was filled and solidified. Subsequently, a 50 cm-wide Teflon bottom plate was inserted below the solidified veratraldehyde at 5 cm. Teflon was chosen since it allows the bottom plate length to be modified according to the state of the artifact on the site. After the bottom plate was inserted, the divers lifted it carefully and covered it with two epoxy-sponge wraps from the top and bottom; next, a self-adhesive bandage was used until the epoxy resin was fully cured [22]. Finally, divers used a buoyancy bag to extract the solidified artefact and transferred it to the laboratory for further research.

3.3. Recovery to the original site process

The extracted artifact was placed inside a dissolving tank, its epoxy-sponge wrap was removed, and 20% (w/w) ethanol solution was poured into the tank. After 48 h, veratraldehyde was totally dissolved. Polypropylene fiber and metal mesh were then removed, and it was revealed that the ship woods had maintained their original condition. Finally, the ethanol solution was gradually replaced with deionized water, and the waterlogged ship woods were soaked and prepared for subsequent protection.

3.4. Analysis methods

3.4.1. Color difference analysis

A colorimeter (CM-2300d, KONICA MINOLTA) was used to detect the color difference changes in the same regions before and after sample solidifying extraction. Based on the CIE 1976 L^* a^* b^* color space, the color coordinates a^*, b^*, and L^* were calculated using a white standard plate for the W1 and W2 samples [23]; four measurement points were used, and each measurement was taken three times. The color difference value was calculated using the following equation:

$$\Delta E* = \left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\right]^{1/2}$$

3.4.2. Micromorphology analysis

The wood microstructure was elucidated using scanning electron microscopy (FEI SIRION-100, Holland) after gold coating for 90 s at an operating voltage of 5.0 kV with a high and low detector.

3.4.3. Residues analysis

The residues of veratraldehyde and its oxidization products on the ship woods were analyzed using nuclear magnetic resonance analysis (^{1}H NMR) after soaking the ship woods in DMSO-d6 for an hour (with Tetramethyl silane as an internal standard). Before that, the samples were dried at a constant temperature of 80 °C for 24 h.

4. Results

4.1. Recording the underwater extraction process

In Fig. 4a–c, several steps involved in the extraction process have been shown. Meanwhile, Fig. 4d–i are the schematics of the different steps. In addition, the state of the ship woods is shown in Fig. 5.

The underwater extraction process can be divided into the following stages. First, after cleaning the sample surface, a stainless-steel mesh was placed around the ship woods (Figs. 4b, e and 5b). Next, some polypropylene fiber clothes were used to cover the sample, and 2 L of melted veratraldehyde was poured onto the sample to achieve solidification. The total duration of the underwater extraction was 42 min, and the two divers consumed an average of 100 MPa of oxygen. In the second stage, 1 L melted veratraldehyde was poured the next day to fill the depression until it completely solidified. This stage lasted 18 min, and the two divers consumed an average of 40 MPa of oxygen. In the third stage, a bottom plate was inserted under the solidified sample, covered with epoxy-sponge, and wrapped with self-adhesive bandages to achieve solidification. This stage lasted 25 min, and the two divers consumed an average of 90 MPa of oxygen. Finally, after the epoxy-sponge was cured, the divers used a buoyancy bag to extract the solidified sample. This stage lasted 18 min, and the two divers consumed an average of 30 MPa of oxygen. Throughout the entire extraction process, a total of 3 L of melted veratraldehyde were used, weighing approximately 3.3 kg.

Video of all phases underwater have been added in the supporting material of this study. Since the amount of oxygen carried by the divers in each phase is fixed and the oxygen consumption

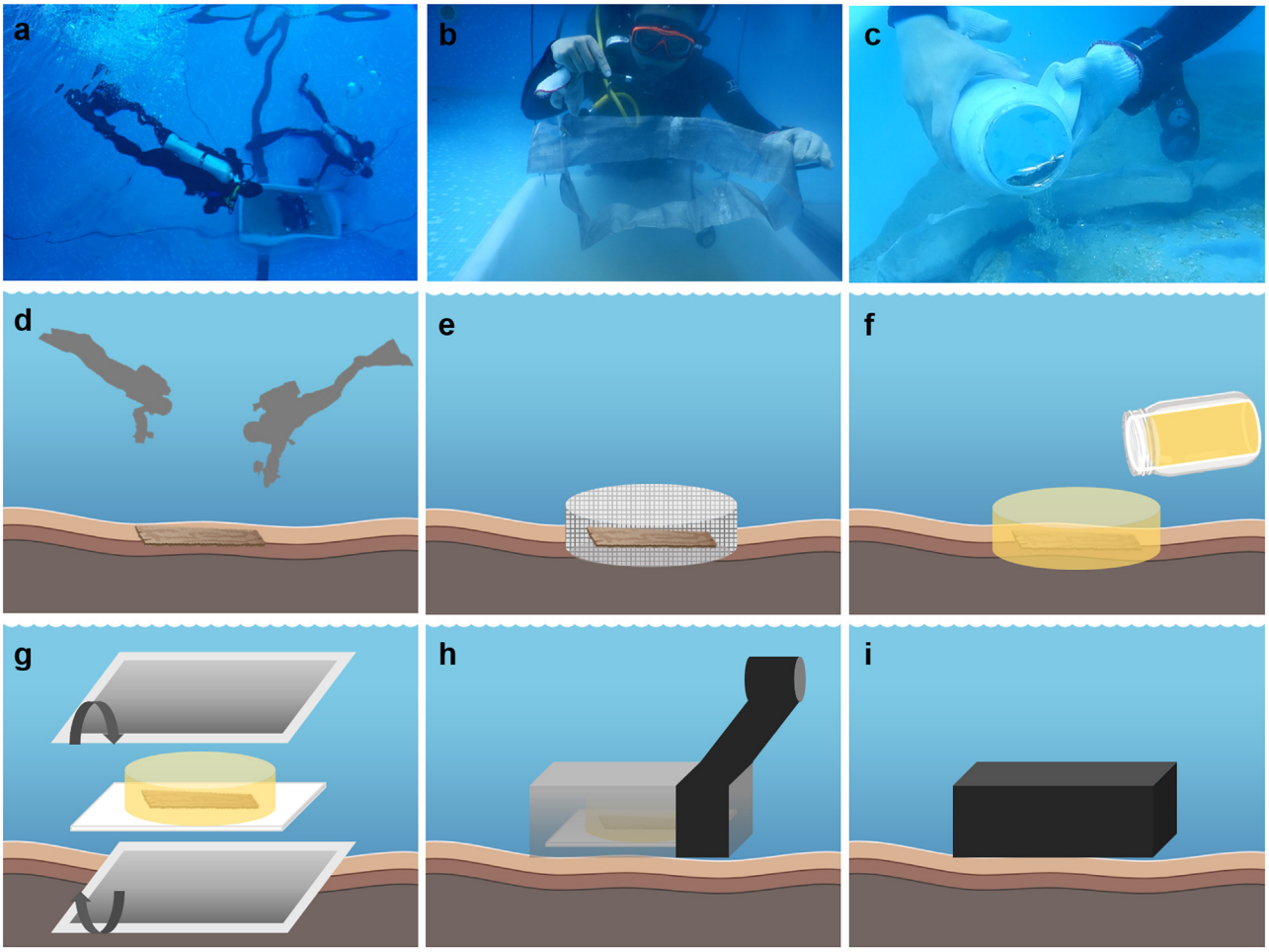

Fig 4. Different steps involved in the underwater extraction at a depth of 7 m (a, d: divers delved to the bottom of the pool with materials for the experiment; b, e: divers inserted the stainless steel mesh; c, f: divers poured the melted veratraldehyde twice until it was completely solidified; g: divers inserted the bottom plate and wrapped it with epoxy-sponge; h: they used self-adhesive bandages to achieve solidification; i: divers placed the solidified sample in a buoyancy bag and waited for extraction).

varies for each task when operating underwater at a depth of 7 m, the total recording time varies for each phase.

Upon comparing the positions of the four ship wood samples before and after extraction, as depicted in Fig. 5a and f respectively, it can be concluded that the original state and position of the samples were accurately replicated. Additionally, it was observed that the lacquer coating on the W1 surface did not undergo significant dissolution, as illustrated in Fig. 5g and h. Moreover, soaking the wood samples in a 20% ethanol solution for 48 h did not result in any noticeable changes in their size.

4.2. The results of color difference analysis

The color difference between the artifacts before and after temporary solidification and extraction is an important factor to evaluate its usefulness. When the color difference ΔE^* <3, the color change cannot be detected by a human eye, indicating that the material has a minor impact on the solidified object; for $3 < \Delta E^* < 5$, although the human eye can detect the color change, it can be permitted in the field of heritage conservation. However, for $5 < \Delta E^*$, the color change is evident [24,25], implying that the material has a significant impact on the solidified object and there may be potential risks. The color difference results for samples W1 and W2 are shown in Fig. 6.

In Fig. 6, it is apparent that ΔE of W2 is slightly higher than 5 for only the bottom left portion; the other data points prove that the change in the surface color of the ship woods solidified by veratraldehyde is not evident. Moreover, the ethanol solution concentration and time period for which the sample is immersed in the solution may be the main causes of color change, which need to be observed in a future work.

4.3. SEM of ship woods after removal

SEM revealed the microstructural features of ship woods before and after temporary solidification. The cross-sectional images (Fig. 7a, c) showed that the cell walls of the wood before solidification were relatively well-preserved, with varying degrees of localized degradation in different regions. Some areas exhibited more severe damage than others. However, after solidification, the microstructural features of the wood (Fig. 7b, d) remain largely unchanged, with intact cell walls and no veratraldehyde crystalline residues found in the pores. A comparison of the radial microstructural features of W1 before and after solidification (Fig. 7e, f) showed that the overall preservation status was good, and some of the original features of the wood were still clearly visible. No apparent crystalline traces were found after solidification. In contrast, the W2 sample exhibited significant aging, with severe degradation and peeling of the cell walls in the central region (Fig. 7g, h). Overall, the microstructural changes before and after temporary solidification of the ship woods were not significant.

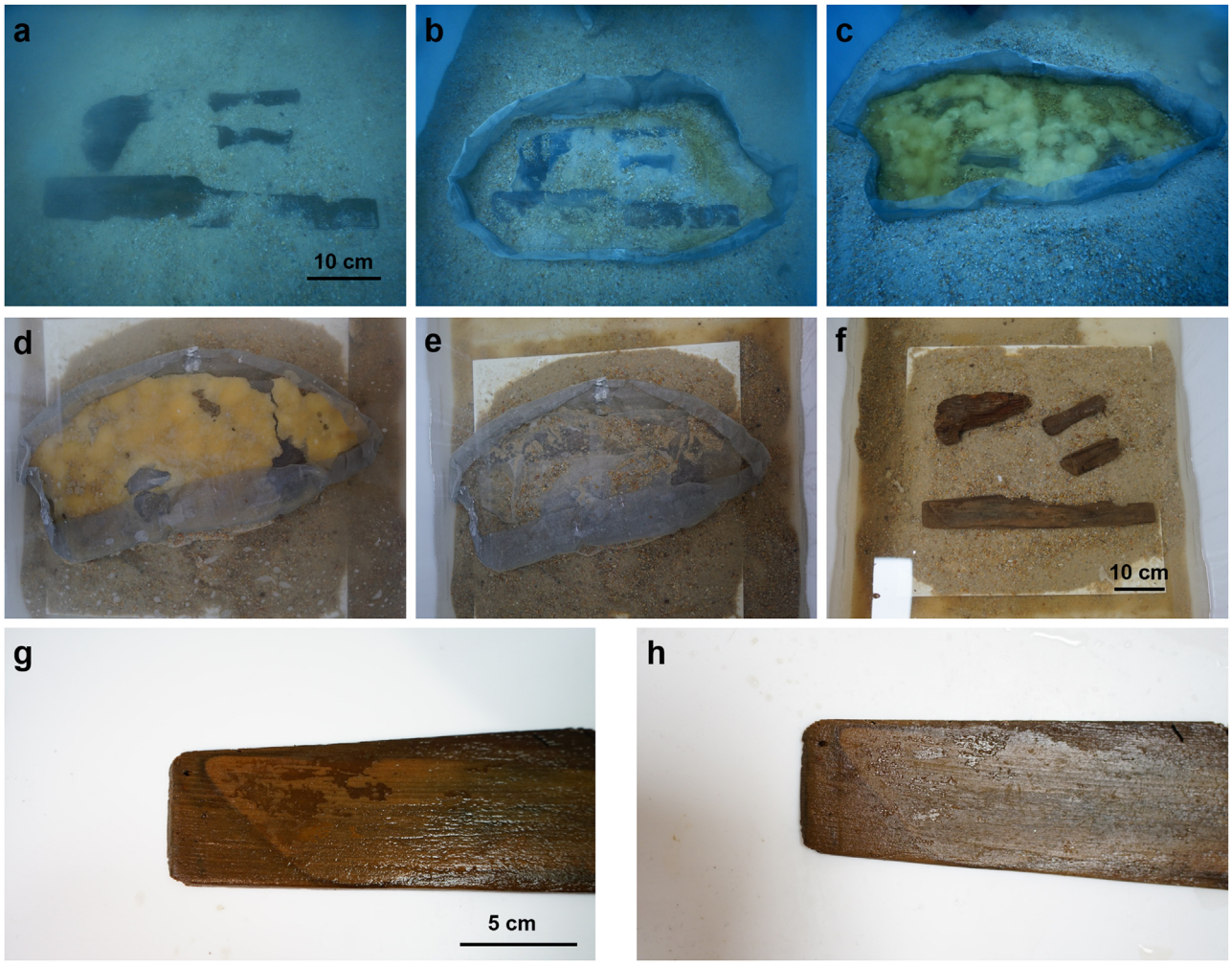

Fig. 5. Image of ship woods before and after extraction (a: the state of ship woods buried underwater, b, c: Images depicting veratraldehyde solidification, d, e: Images depicting solidification dissolution, f: extracted ship woods, g, h: difference in W2 before and after extraction).

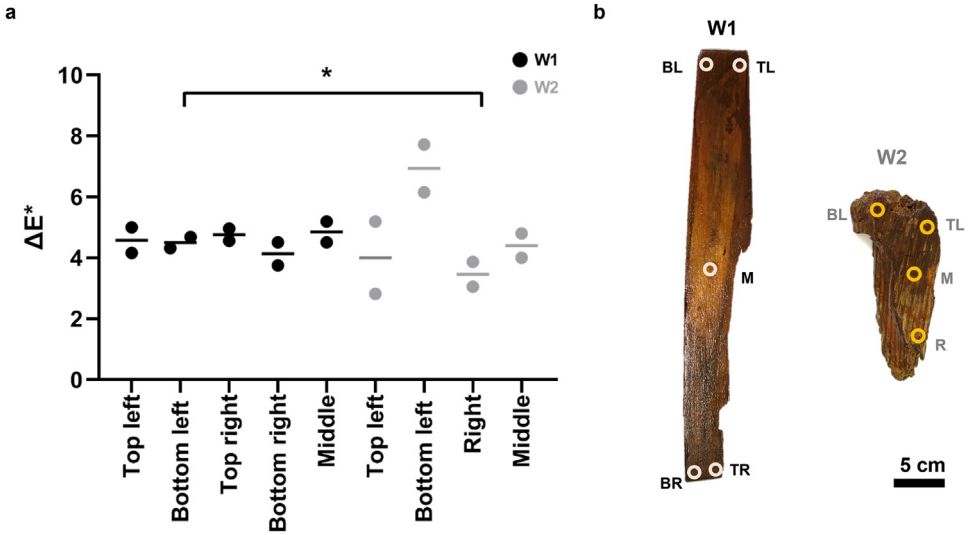

Fig. 6. Results of the color difference of samples W1 and W2 (a: the results of color difference test, b: the location photos of color difference test).

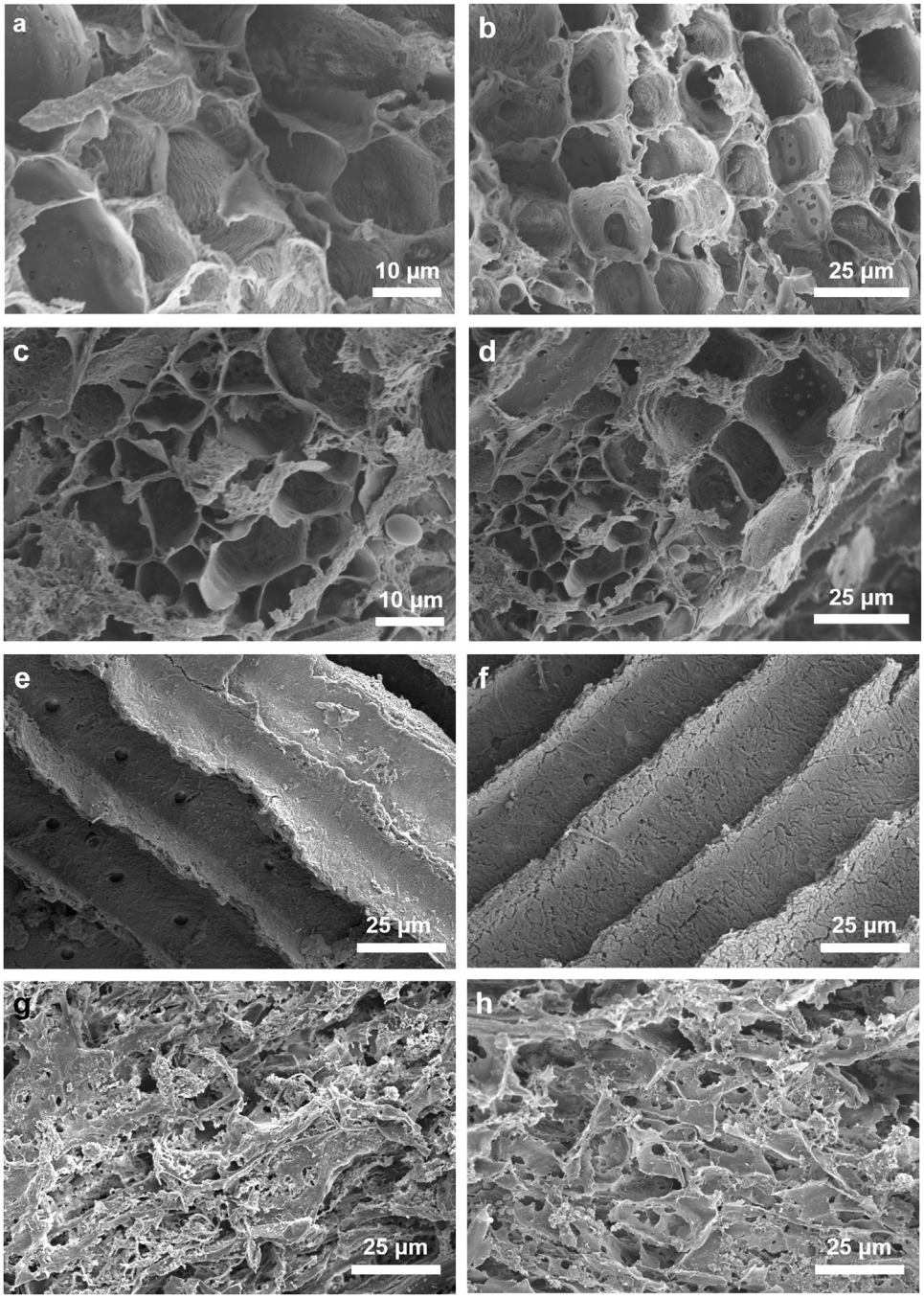

Fig. 7. SEM of ship woods before and after solidification (a: W1 sample before solidification, cross-section, b: W1 sample after solidification, cross-section, c: W2 sample before solidification, cross-section, d: W2 sample after solidification, cross-section, e: W1 sample before solidification, f: W1 sample after solidification, g: W2 sample before solidification, h: W2 sample after solidification).

4.4. Residue analysis

We carried out ^{1}H NMR to determine whether there were any traces of veratraldehyde and other oxidation products remaining on the samples, and the results were presented in Fig. 8. The ^{1}H NMR (500 MHz, DMSO-d6) of pure veratraldehyde (Fig. 8a) (δ 9.83 (s, 1H), 7.53 (d, J = 9.7 Hz, 1H), 7.37 (d, J = 1.4 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 3.84 (d, J = 19.6 Hz, 6H), 3.39 (s, 1H)), showed three hydrogen peaks with chemical shift values of 7.53, 7.37, and 7.14 ppm, representing the three other hydrogens on the benzene ring. The chemical shift at 9.84 ppm corresponds to the hydrogen on the aldehyde group. The sharp peaks at 3.84 and 3.39 ppm were attributed to the two methoxy groups, and the peak at 2.5 ppm represented the solvent peak of DMSO-d6.

The extracted ship woods were analyzed and showed the following results (Fig. 8b): δ 3.32 (s, 1H), 2.50 (s, 1H). The hydrogen peaks on the benzene ring were represented by the chemical shift values of 3.87 and 3.83, indicating the presence of veratraldehyde. However, after exchanging the ethanol solution once every 48 h and waiting for 6 days, we observed that the hydrogen peaks had completely disappeared, indicating that the removal process has been completed.

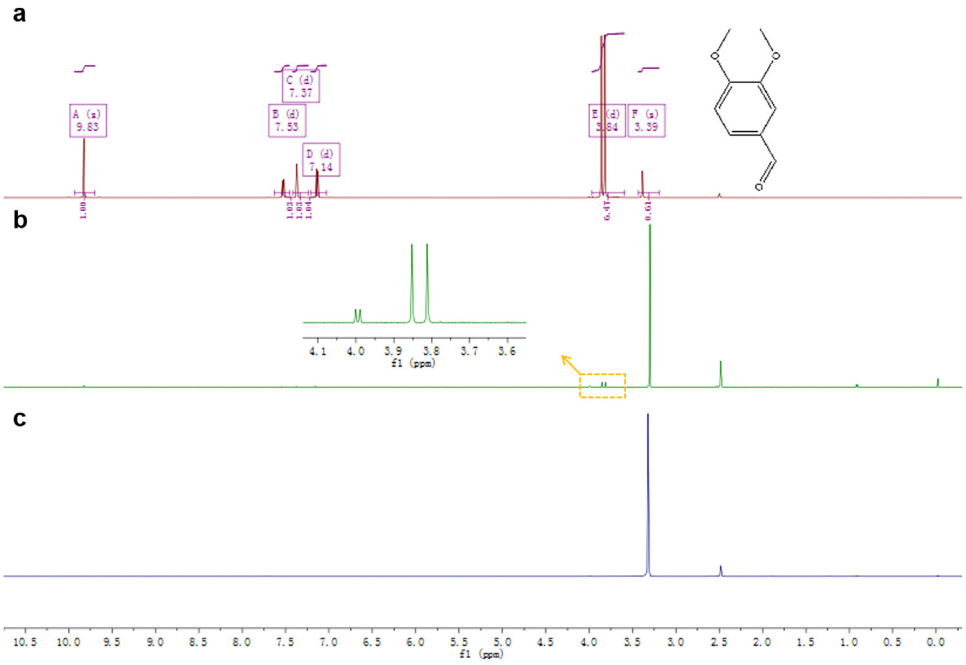

Fig. 8. Results of the ^{1}H NMR analysis (a: ^{1}H NMR results of veratraldehyde, b: ^{1}H NMR results of the ship wood samples after solidification, c: ^{1}H NMR results of ship wood samples after waiting for 6 days).

5. Conclusions

This study was designed to determine whether veratraldehyde and its supporting equipment can be used in underwater archaeological applications. Multiple analyses revealed that the proposed extraction method can safely extract the fragile ship woods underwater (up to a depth of 7 m), while fully maintaining their original buried state; this implies that information contained in these artifacts can be preserved.

Currently, the proposed underwater extraction experiment requires four dives, with a total of 118 min of underwater work (including prepare time underwater). The average oxygen consumption for each dive is estimated to be 65 MPa. Furthermore, the analysis results suggest that the color of the wood did not change, lacquer remained intact, and microstructure did not change, indicating that the extraction process will not damage fragile artifacts. Meanwhile, dissolution of veratraldehyde using a lower-concentration ethanol solution will ensure that the organic artifacts are not damaged. Although a very small amount of veratraldehyde residue was left, this residue also evaporates completely under natural conditions due to the high saturated vapor pressure of veratraldehyde.

CRediT authorship contribution statement

Xinxin Wang: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Hao Wang:** Formal analysis, Funding acquisition, Investigation, Methodology, Writing – review & editing. **Bingjian Zhang:** Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing. **Yulan Hu:** Project administration, Resources, Writing – review & editing. **Longguan Zhu:** Funding acquisition, Writing – review & editing.

Acknowledgement

National Key R&D Program of China (2020YFC1520504) are greatly acknowledged for their financial support.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.05.012.

References

[1] C.J.S. Forrest, Defining 'underwater cultural heritage, Int. J. Nautical Archaeol. 31 (2002) 3–11.
[2] X.Q. Chen, K. Xia, W.J. Hu, M. Cao, K. Deng, S.Q. Fang, Extraction of underwater fragile artifacts: research status and prospect, Herit. Sci. 10 (2022) 9, doi:10.1186/s40494-022-00645-1.
[3] X.Q. Chen, B. Zhang, Z. Zhang, Application of veratraldehyde as a temporary consolidant for relics at underwater cultural heritage sites, Archaeometry 61 (2019) 1417–1429.
[4] M.J. Aznar, In situ preservation of underwater cultural heritage as an international legal principle, J. Maritime Archaeol. 13 (2018) 67–81.
[5] M.J. Aznar-Gomez, Treasure Hunters, Sunken state vessels and the 2001 UNESCO convention on the protection of underwater cultural heritage, Int. J. Mar. Coast. Law 25 (2010) 209–236.
[6] U. Koschtial, The 2001 UNESCO convention on the protection of the underwater cultural heritage: advantages and challenges, Museum Int. 60 (2008) 63–69.
[7] M.Z.M. Nor, A. Zahid, Competing interests in the underwater cultural heritage: a question of balance, J. East Asia Int. Law 9 (2016) 121–135.
[8] S.S. Wu Jiancheng, Zhang Yongqiang, Whole salvage of Sunken ancient vessel Nanhai no.1, Ship Ocean Eng. 37 (2008) 65–68.
[9] B.D. Petriaggi, D.J. Gregory, J. Dencker, Recovery of fragile objects from underwater archaeological excavations: new materials and techniques by SASMAP project, in: 5th EuroMed International Conference, Amathus, CYPRUS, 2014, pp. 625–634.
[10] B. Lu, S. Zhou, China's state-led working model on protection of underwater cultural heritage: practice, challenges, and possible solutions, Mar. Policy 65 (2016) 39–47.
[11] S. Khakzad, K. Van Balen, Complications and effectiveness of in situ preservation methods for underwater cultural heritage sites, Conserv. Manage. Archaeol. Sites 14 (2012) 469–478.
[12] S. Rowe, C. Rozeik, The uses of cyclododecane in conservation, Stud. Conserv. 53 (2008) 17–31.
[13] C. Rozeik, The treatment of an unbaked mud statue from ancient Egypt, J. Am. Inst. Conserv. 48 (2009) 69–81.
[14] M. Brown, A. Davidson, The use of cyclododecane to protect delicate fossils during transportation, J. Vertebr. Paleontol. 30 (2010) 300–303.
[15] D. Vernez, B. Wognin, C. Tomicic, G. Plateel, N. Charriere, S. Bruhin, Cyclododecane exposure in the field of conservation and restoration of art objects, Int. Arch. Occup. Environ. Health 84 (2011) 371–374.
[16] J.X. Han, The use of menthol on the archaeological site at the mausoleum of the first Qin Emperor, Stud. Conserv. 59 (2014) S223–S224.

[17] X. Han, B. Rong, X. Huang, T. Zhou, H. Luo, C. Wang, The use of menthol as temporary consolidant in the excavation of Qin Shihuang's Terracotta Army, Archaeometry 56 (2014) 1041–1053.
[18] X.Q. Chen, L. Xie, F. Wang, Y. Wu, B. Zhang, L. Zhu, Temporary consolidation and packaging of fragile cultural relics at underwater archaeological sites to maintain their original state during extraction, Archaeometry 62 (2020) 1067–1077.
[19] F. Wang, X. Chen, X. Wang, B. Zhang, Y. Hu, L. Zhu, Technique of temporary undisturbed reinforcement extraction of fragile lacquerware from shipwrecks, J. Maritime Archaeol. 16 (2021) 27–38.
[20] X. Wang, B. Zhang, Y. Hu, L. Zhu, Temporary solidifying extraction and in-situ preservation of fragile marine wooden artifacts: experimental study and pilot test, J. Cult. Herit. 53 (2022) 220–225.
[21] X. Wang, B. Zhang, Y. Hu, Research on extraction of fragile bamboo slips by underwater temporary solidification in original state, J. Cult. Herit. 51 (2021) 174–181.
[22] X.-.Q. Chen, B. Zhang, Z. Zhang, A novel method of temporary solidification and extraction of underwater fragile relics in their original state, Int. J. Adhes. Adhes. 104 (2021) 102724, doi:10.1016/j.ijadhadh.2020.102724.
[23] P. Korytkowski, A. Olejnik-Krugly, Precise capture of colors in cultural heritage digitization, Color Res. Appl. 42 (2017) 333–336.
[24] O. Garcia, K. Malaga, Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials, J. Cult. Herit. 13 (2012) 77–82.
[25] J.D. Rodrigues, A. Grossi, Indicators and ratings for the compatibility assessment of conservation actions, J. Cult. Herit. 8 (2007) 32–43.

Journal of Cultural Heritage 53 (2022) 220–225

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

Temporary solidifying extraction and in-situ preservation of fragile marine wooden artifacts: Experimental study and pilot test

Xinxin Wang[a], Bingjian Zhang[a,b,*], Yulan Hu[a], Longguan Zhu[b]

[a] Department of Cultural Heritage and Museology, Zhejiang University, Hangzhou, 310028, PR China
[b] Department of Chemistry, Zhejiang University, Hangzhou, 310027, PR China

ARTICLE INFO

Article history:
Received 26 September 2021
Accepted 24 December 2021
Available online 5 January 2022

Keywords:
Fragile marine artifacts
"*Nanhai I*" shipwreck remnants
Temporary solidification
Veratraldehyde
Pilot test

ABSTRACT

Previous studies have found that the temporary consolidant veratraldehyde, which is denser than water, can be used for solidifying and extracting fragile submerged artifacts. However, whether veratraldehyde can be effectively used for in-situ artifact extraction in marine archaeology requires further study. Here, we systematically discuss the effects of seawater salinity, water temperature, and hydrostatic pressure on the veratraldehyde solidification rate, as well as the development of a double-layer insulating bottle that can prevent molten veratraldehyde from solidifying within an hour, the construction of a stainless steel mesh fence, in-situ packaging materials for fragile submerged artifacts, and the veratraldehyde recycling method. Further, the marine environment was simulated and "*Nanhai I*" shipwreck remnants were used as fragile marine artifacts in a pilot test on in-situ extraction.

© 2021 Elsevier Masson SAS. All rights reserved.

1. Introduction and research aim

Integral salvage operations and in-situ extraction of fragile artifacts remain a challenge, especially in the marine environment. After been buried in seabed for decades or even hundreds of years, organic artifacts especially wooden artifacts are basically waterlogged, and the cellulose is degraded by microbial decomposition causing the severely decayed and fragile as well. For example, the salvage operations of the Southern Song sunken vessel "*Nanhai I*" in China, the oldest and the most integrally preserved shipwreck in the world, in 2007 used a steel open caisson, which preserved the sunken vessel and its load but required huge human and financial resources [1,2]. This method is also not applicable to fragile artifacts scattered on the seabed.

In terrestrial archaeology, temporary consolidants such as cyclododecane and menthol have been widely used in the extraction of fragile artifacts because of their good solidification effect, volatile removal, and no solidification residue [3–5]. However, since these materials are less dense than water, they cannot be solidified underwater. Recent studies have identified veratraldehyde, a volatile material with a density greater than water, which can be used for temporary solidifying and extraction of underwater artifacts made of wood, stone, pottery, and iron [6], but these studies are limited to small-scale experiments [7–9]. Questions about the use of veratraldehyde in marine archaeology include: Do the salt concentration and seawater temperature affect veratraldehyde solidification? Do changes in hydrostatic pressure at different depths in the ocean alter the veratraldehyde solidification rate? How can molten veratraldehyde be effectively maintained when transported underwater? What additional materials can divers use to safely pack and extract large and fragile artifacts? Finally, with respect to improve material utilization, how to recover and recycle used veratraldehyde?

To answer these questions, this study aimed at the extraction of fragile marine artifacts and performed experimental research on a series of problems related to the application of veratraldehyde. In addition, a pilot test was performed on the in-situ extraction of fragile artifacts using nine pieces of ship wood at the wreckage site of the sunken vessel "*Nanhai I*", providing practical information for the application of veratraldehyde in marine archaeology.

2. Materials and methods

Veratraldehyde (3,4-dimethoxybenzaldehyde), with a density slightly greater than seawater (i.e., 1.1708 g/cm^{-3}), melts to a pale yellow liquid when heated to 43 °C [10,11]. It can solidify under water in a few minutes and has a certain degree of adhesion to sand, pottery, iron, wood, and other materials in water. Solidified veratraldehyde can also be dissolved by an ethanol solution or evaporated.

The main experimental instruments used were an electronic analytical balance, constant temperature water bath, Fourier transform infrared (FT-IR) spectrum analyzer, CTM 2500 universal ma-

* Corresponding author.
E-mail address: zhangbiji@zju.edu.cn (B. Zhang).

https://doi.org/10.1016/j.culher.2021.12.006
1296-2074/© 2021 Elsevier Masson SAS. All rights reserved.

terial testing machine (Xieqiang, China), sand suction device (Suisaku, Japan), rotary evaporator, and high-pressure reactor.

The samples were all waterlogged wood from "*Nanhai I*" shipwreck (K4NH-3), and were placed in deionized water without any treatment right after extraction.

2.1. Effect of water temperature and NaCl concentration on the veratraldehyde solidification rate

A fine sand layer was spread on the bottom of a 50-ml plastic cup, and 20 ml of NaCl solution was added at different concentrations (0–3.5%, the average NaCl concentration in seawater is 3.0%) [12,13]. Moreover, the temperature of the water bath was controlled (8–24 °C) [14,15], 1 ml of molten veratraldehyde was added to water each time, and the solidification time was recorded. With water temperature and NaCl concentration as variables, a two-factor orthogonal experiment was designed and conducted.

2.2. Effect of hydrostatic pressure on veratraldehyde solidification rate

Since pressure increases with water depth, experiments were performed using a high-pressure reactor to test the effect of hydrostatic pressure changes on the veratraldehyde solidification rate [16]. The maximum depth of underwater archaeology is approximately 30 m; therefore, the relative pressure range of the reactor was set between 0 and 0.3 MPa [17].

Accurately measured 20 ml of water was placed in the Teflon liner of the reactor, and 5 ml of molten veratraldehyde under water was added each time. The liner was put back, and compressed air was applied for 5 min. The reactor was then opened, and solidified veratraldehyde was weighed and the percentage of solids was calculated.

2.3. Insulating bottle design and performance test

In the actual process of extracting fragile submerged artifacts, molten veratraldehyde must not solidify before the divers can reinforce the artifacts. Therefore, we constructed a double-layer insulating bottle—the inner container was filled with molten veratraldehyde, the middle compartment was insulated to reduce heat transfer, and the outer container was made of polypropylene for compressive strength.

The insulating materials selected were as follows: (1) Polyurethane coating: The thermal conductivity of this material is 0.03 W/m• °C, with good thermal insulation and cost performance [18]. It is the most commonly used thermal insulating coating at present [19]. (2) Composite silicate coating: This thermal barrier coating has a microporous mesh structure and is widely used in pipe wall insulation [20,21]. (3) Foam and strap: This is a physical method of increasing the lining thickness to improve the thermal insulating effect.

2.4. Contact angle test of shape-shifting metal fence

To minimize the amount of veratraldehyde used, a metal mesh was designed as a fence. According to shape, the artifacts to be extracted were surrounded to restrain molten veratraldehyde within the metal mesh fence, and the whole structure was solidified and extracted. This method of using a metal mesh fence can permit shape-shifting according to the size of submerged artifacts, can be easily constructed compared with a plastic frame, and can substantially reduce the amount of veratraldehyde used.

Considering metal strength and preventing veratraldehyde leakage, copper mesh and stainless steel mesh with mesh number between 80 and 150 were selected as fences in the experiment. The contact angle of molten veratraldehyde on the surface of different metal meshes was tested to select the appropriate metal mesh fence.

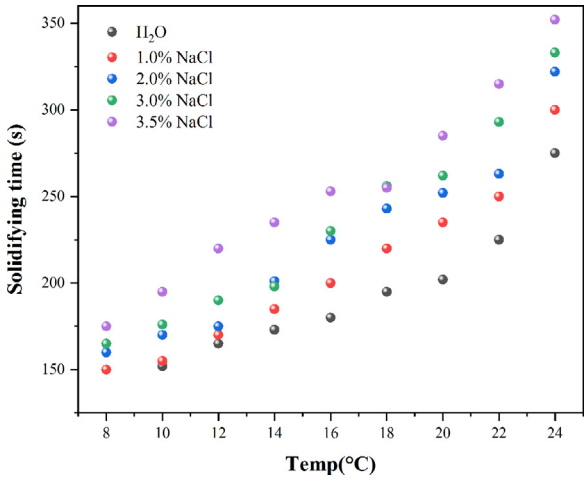

Fig. 1. Veratraldehyde solidification rate under different conditions.

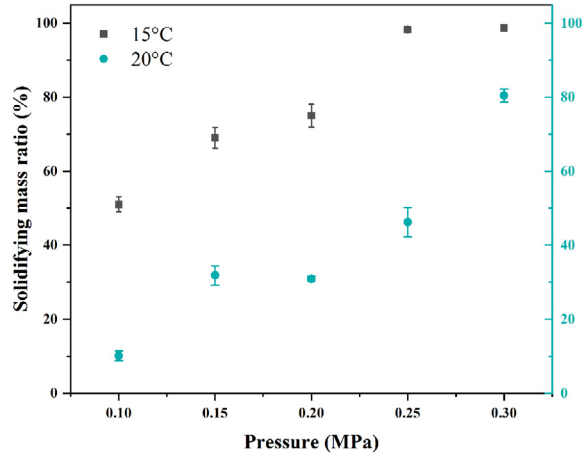

Fig. 2. Veratraldehyde solidification mass ratio at different pressures (within 5 min).

2.5. Veratraldehyde recovery experiment

Because of the high consumption of veratraldehyde in extracting fragile artifacts, its recovery is necessary to improve material utilization. The temporary veratraldehyde-reinforced structure was placed in a 30% ethanol solution to dissolve veratraldehyde and restore the artifact to its original state. The resulting mixture was placed in the pear-shaped bottle of a rotary evaporator and evaporated in vacuo at 70 °C. The reaction was stopped after 30 min. To verify whether rotary evaporation can oxidize veratraldehyde, the concentrated solution obtained by rotary evaporation and the solidified product were collected, analyzed by FT-IR, and compared separately.

3. Results and discussion

3.1. Effect of water temperature and NaCl concentration on veratraldehyde solidification

Fig. 1 shows the veratraldehyde solidification rate under different conditions of water temperature and NaCl concentration.

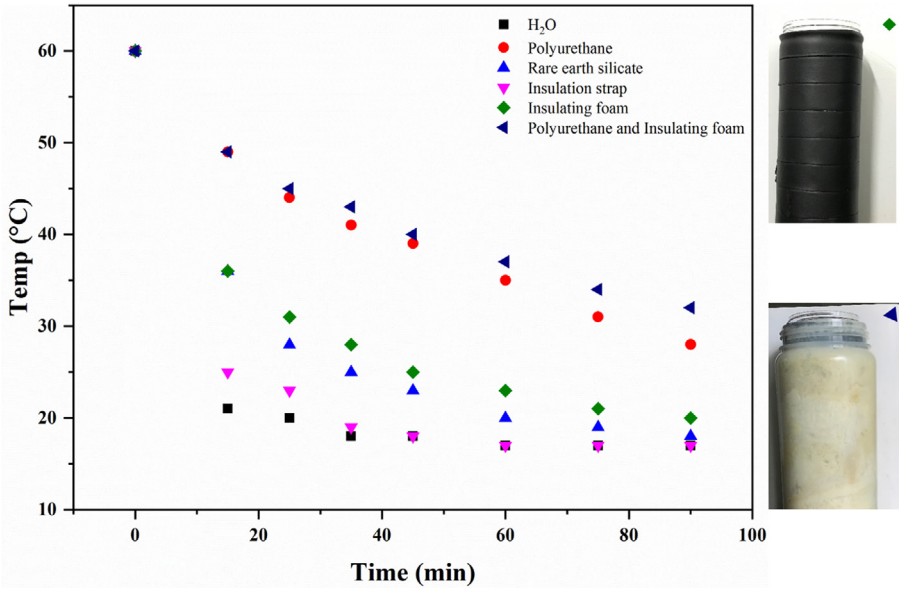

Fig. 3. Effect of insulating materials (used alone or in combination) on rate of change in water temperature.

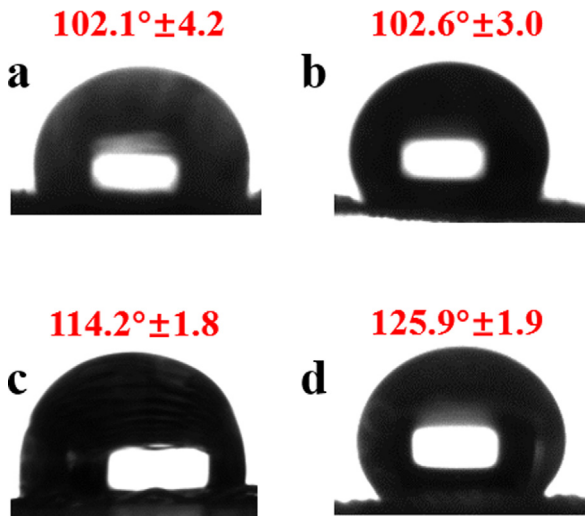

Fig 4. Contact angle between different metal fence and veratraldehyde underwater (a: 80 mesh copper fence, b: 80 mesh 304 stainless steel fence, c: 100 mesh 304 stainless steel fence, d: 150 mesh 304 stainless steel fence).

As the temperature of the solution increases, the veratraldehyde solidification rate increases from 62.5% to 112.5%. Also, higher NaCl concentration resulted in a longer solidification time, and the veratraldehyde solidification rate increased by about 75 s in seawater (3.5% NaCl) compared with pure water.

This may be because the increase in temperature enhanced the saturation of the entire solution, which is not conducive to solidification [22], thus leading to an increase in the veratraldehyde solidification rate. Changing the NaCl concentration in the solution at a constant temperature also affects the veratraldehyde solidification rate under water to a certain extent. This is because an ionization effect is produced to inhibit the growth of the crystal core after it adsorbs ions, and this phenomenon becomes more pronounced with the increase of temperature.

3.2. Effect of pressure on veratraldehyde solidification

Fig. 2 shows the veratraldehyde solidification mass ratio at different pressures within 5 min.

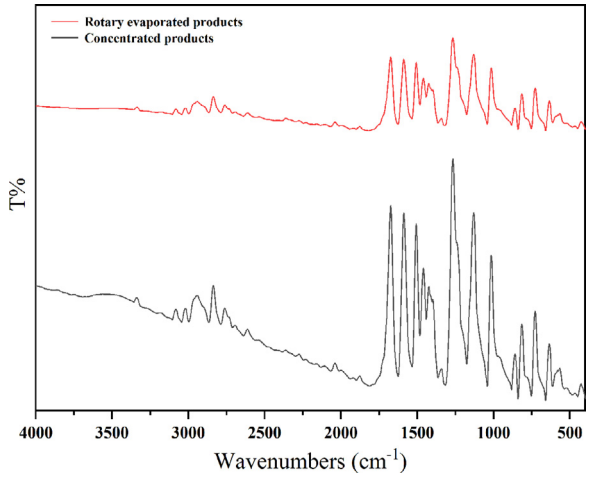

Fig. 5. FT-IR plots of concentrated and evaporated products obtained by rotary evaporation of veratraldehyde–ethanol solution.

As hydrostatic pressure increases, veratraldehyde solidifies faster, indicating that the deep water environment will cause molten veratraldehyde to solidify faster. The solidification rate increases by about 50% at a depth of 30 m. This increase in the solidification rate is mainly because subcooling of the veratraldehyde crystal increases with pressure and spontaneous nucleation is more likely to occur [23,24].

3.3. Effect of insulating materials on veratraldehyde solidification

Fig. 3 shows the effect of four insulating materials used alone or in combination as an insulating layer in the construction of the insulating bottle. The rate of change in water temperature in the inner container was used to measure the insulation effect. Polyurethane has a better insulating effect among the insulating materials, and foam has a better insulating effect among the packaging materials. Therefore, polyurethane was combined with insulating foam. The foam was first wrapped around the inner container, and the space between the inner and outer containers was then filled with polyurethane, resulting in an optimal insulating effect.

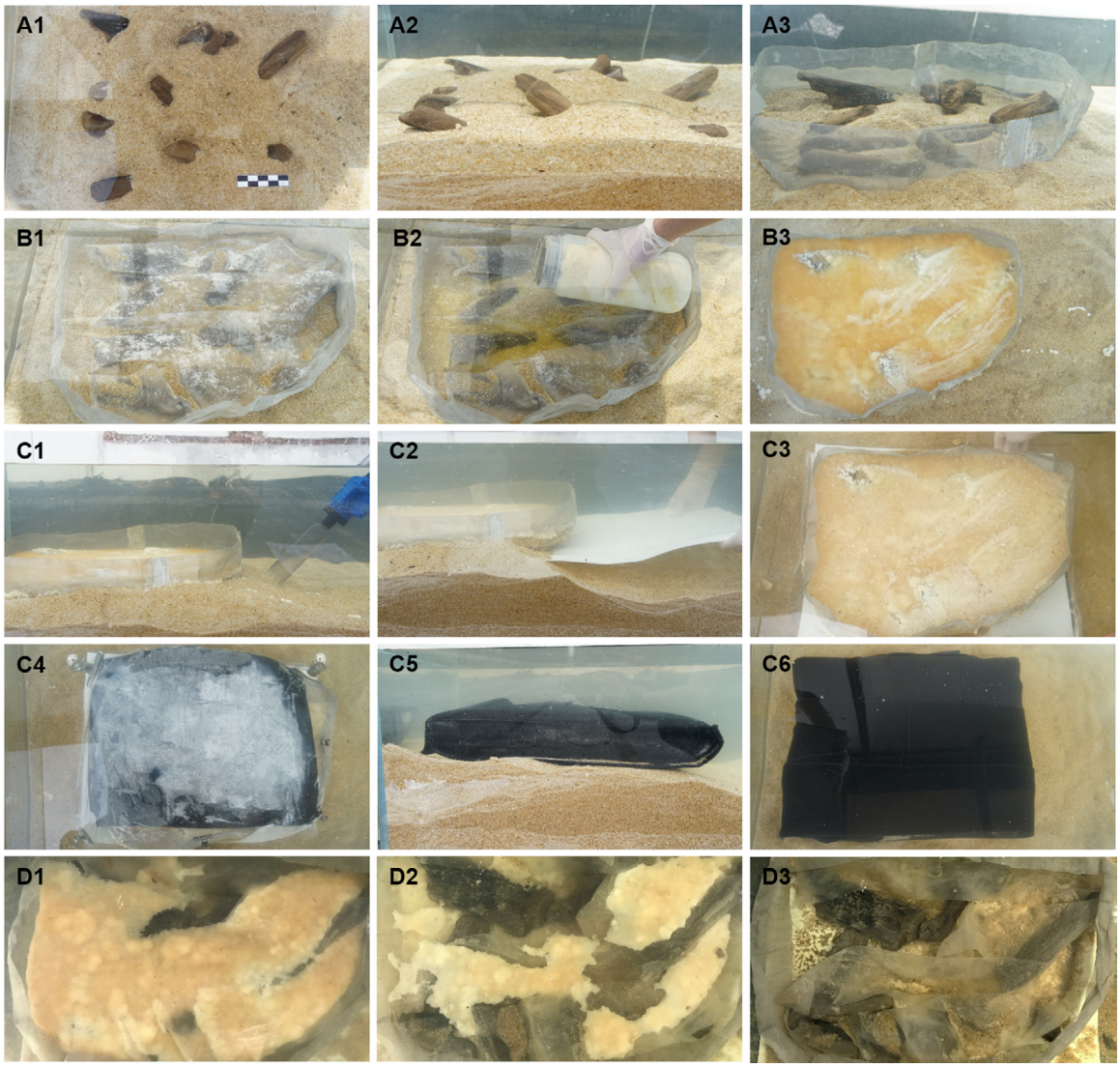

Fig. 6. Important steps in the pilot test. (A1–3: Simulation of artifacts, B1–3: Solidification of artifacts, C1–3: Insertion of bottom plate, C4–6: Packaging of whole artifact structure, D1–3: Restoration of artifact structure).

Thus, this bottle insulated with polyurethane and foam prevented molten veratraldehyde from solidifying in an hour, fully meeting the requirements of heat preservation and anti-consolidation of molten veratraldehyde when extracting fragile artifacts from the seabed.

3.4. Contact angle test of shape-shifting metal fence

Anti-leakage was determined by testing the contact angle of molten veratraldehyde on different fence materials. The contact angle of molten veratraldehyde on the metal mesh decreases with mesh size. A smaller contact angle implies better wettability, which leads to the penetration of molten veratraldehyde by spreading on the metal surface (Fig. 4). When the mesh size increases, molten veratraldehyde is less likely to penetrate, but the metal mesh will be softer, leading to a decrease in its strength. Hence, a 100-mesh 304 stainless steel fence was selected as the shape-shifting metal fence.

3.5. Composition analysis of veratraldehyde recovered products

Veratraldehyde was recovered by rotary evaporation according to the reaction conditions, and FT-IR analysis of the concentrated and evaporated products showed that IR spectra matched the standard spectra of veratraldehyde: both showed a strong band at 1690–1700 cm^{-1} (because of the carbonyl stretch) and two bands of moderate intensity in the 2700–2800 cm^{-1} region (because of the H-C = O stretch in aldehydes only; Fig. 5) [10,25]. Therefore, the recovered products remained unchanged. This indicates that rotary evaporation at 70 °C does not alter the chemical composition of veratraldehyde and does not affect its recycling.

4. Pilot test of underwater reinforcement extraction

Marine submerged artifacts mainly exist in the buried or semi-buried state, which is different from laboratory simulation experiments [26]. Considering seawater characteristics and artifact distribution, a pilot test was performed to determine the general reinforcement extraction steps for various practical applications.

4.1. Insulating bottle for molten veratraldehyde

The solidifying agent molten veratraldehyde should be kept completely sealed and insulated during diving to ensure that it does not solidify before reaching the seabed. Therefore,

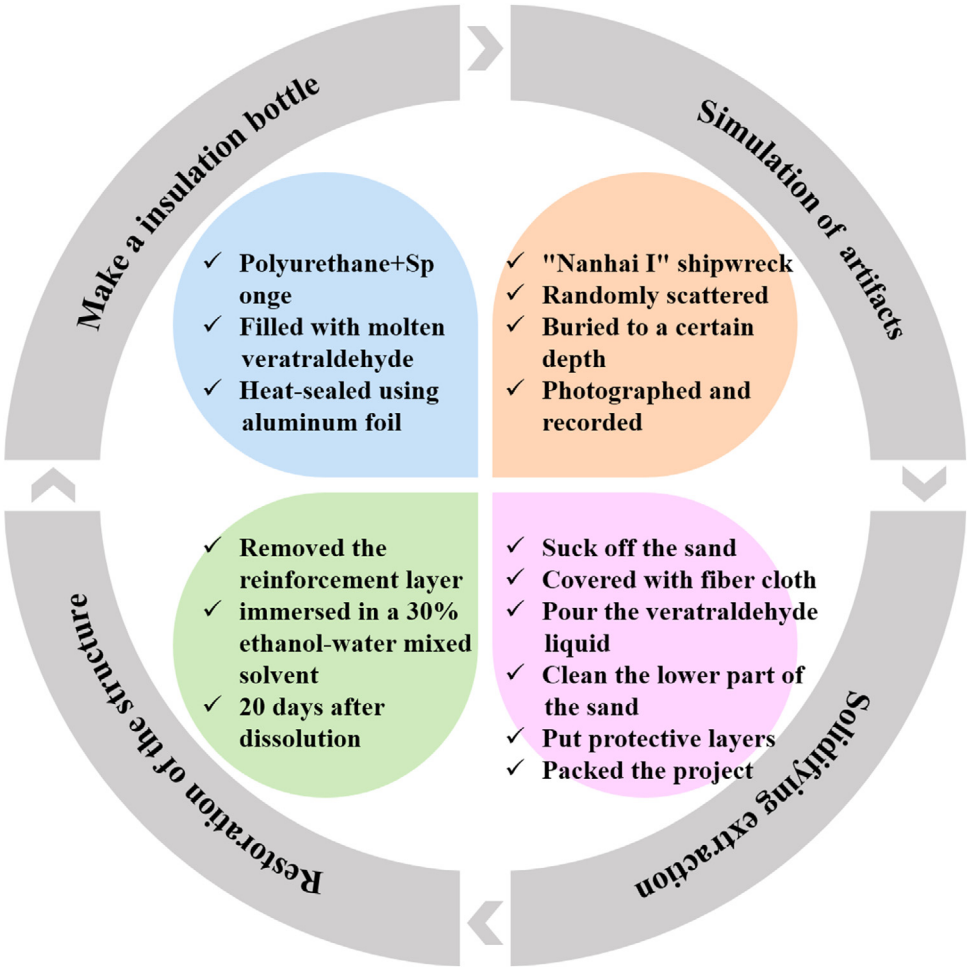

Fig. 7. Pilot test flowchart.

polyurethane and foam were used to construct a double-layer insulating bottle. A layer of insulating foam was wrapped around the inner container, and polyurethane (A:B, 1:2) was injected into the space between the inner and outer containers. The inner container was filled with molten veratraldehyde and heat-sealed using aluminum foil to ensure the bottle was tightly closed. When the aluminum foil is pierced underwater, molten veratraldehyde will flow out and solidify on the surface of the artifact.

4.2. Simulation of submerged artifacts

In this experiment, nine pieces of ship wood (K4NH-3) of different sizes from the "*Nanhai I*" shipwreck, which were either scattered on the seabed or buried to a certain depth, were used to simulate large fragile submerged artifacts, and the sites were photographed and recorded.

To study extraction techniques at the original site, a simulated artifact structure (length 47 cm; height 38 cm) was used as the pilot test subject and a 3.5% NaCl aqueous solution was used to simulate seawater for the reinforcement extraction experiment (Fig. 6A1).

4.3. Reinforcement extraction experiment

A sand suction device was used to remove the sand on the surface of the submerged artifacts, and the artifacts were then cleaned with a brush so that the artifact surfaces were partially exposed (Fig. 6A2). A 100-mesh 304 stainless steel fence (length 160 cm; width 15 cm) was selected according to the artifact size, and its ends were firmly fixed with epoxy glue to construct a shape-shifting metal fence that could surround the submerged artifact. A polypropylene fiber cloth that can absorb molten veratraldehyde was used to cover the surface (Fig. 6B1). The aluminum foil seal of the double-layer insulating bottle was then pierced, and the veratraldehyde liquid was poured into the metal fence (Fig. 6B2) until it covered the entire artifact structure and solidified naturally (Fig. 6B3).

After complete veratraldehyde solidification, the sand suction device was used to clean the lower part of sand from one end of the solidified artifact structure to provide space for insertion of the bottom plate. A 5-mm polytetrafluoroethylene board was then inserted about 20 mm from the bottom, and a pre-prepared polyurethane foam–epoxy glue protective layer was applied to the bottom plate and the frame before clips were fixed (Figs. 6C4 and C5). Furthermore, the whole structure was packaged and secured with self-adhesive tape. After the epoxy glue within the foam solidifies naturally, the whole structure has good collision resistance [27] and can be smoothly extracted from underwater and transferred to the laboratory (Fig. 6C6).

4.4. Restoration of the artifact structure

After removing the self-adhesive tape and external protective layer, the veratraldehyde–ship wood solidified artifact structure was immersed in a 30% ethanol solution. After 20 days of disso-

lution, veratraldehyde was completely removed, and each artifact was preserved intact as in the original condition (Fig. 6D1–3).

5. Conclusions

In this study, experimental exploration on the application of veratraldehyde in the temporary reinforcement of marine submerged artifacts was conducted. The effects of NaCl concentration, temperature, pressure, and other factors on the veratraldehyde solidification rate were also studied. Further, the large amount of used veratraldehyde was recycled Figure 7.

In addition, a set of practical reinforcement methods and supporting equipment was designed, and a pilot test was performed using "*Nanhai I*" shipwreck remnants as a temporary reinforcement structure. Although the pilot test used only wood from the shipwreck, the findings can provide preliminary data for future practical applications in marine archaeology.

Acknowledgement

National Key R&D Program of China (2020YFC1520504) are greatly acknowledged for their financial support.

References

[1] W.U. Jian-cheng, Z. Yong-qiang, The integral salvage of ancient sunken vessel Nanhai I, J. Navig. China 31 (2008) 383–387 ,399.
[2] W.U. Jian-cheng, Whole salvage scheme for ancient sunken vessel "Nanhai No 1", Guangdong Shipbuild. 3 (2004) 69–72.
[3] X.H.H. Luo, X. Huang, W. Li, Progress in uses of cyclododecane in art conservation, Materials China 31 (2012) 48–55.
[4] X.H.X. Han, B.J. Zhang, Laboratory research into the use of menthol as a temporary consolidant for conservation on archaeological excavations, Archaeometry 60 (2018) 1334–1345.
[5] B.R.X. Han, The use of menthol as temporary consolidant in the excavation of Qin Shihuang's Terracotta Army, Archaeometry (2014) 1041–1053.
[6] L.X.X.Q. Chen, F. Wang, Y. Wu, B. Zhang, L. Zhu, Temporary consolidation and packaging of fragile cultural relics at underwater archaeological sites to maintain their original state during extraction, Archaeometry 62 (2020) 1067–1077.
[7] X.C F. Wang, X. Wang, B. Zhang, Y. Hu, L. Zhu, Technique of Temporary Undisturbed Reinforcement Extraction of Fragile Lacquerware from Shipwrecks, J. Maritime Archaeol. 16 (2021) 27–38.
[8] X.Q. Chen, B. Zhang, Z. Zhang, Application of veratraldehyde as a temporary consolidant for relics at underwater cultural heritage sites, Archaeometry 61 (2019) 1417–1429.
[9] X.Q. Chen, B.J. Zhang, Z.G. Zhang, A novel method of temporary solidification and extraction of underwater fragile relics in their original state, Int. J. Adhes. Adhes. 104 (2021) 6.
[10] J. Molleti, G.D. Yadav, Green synthesis of veratraldehyde using potassium promoted lanthanum magnesium mixed oxide catalyst, Org Process Res Dev 21 (2017) 1012–1020.
[11] M. Melian-Rodriguez, S. Saravanamurugan, S. Kegnaes, A. Riisager, Aerobic oxidation of veratryl alcohol to veratraldehyde with heterogeneous ruthenium catalysts, Top. Catal. 58 (2015) 1036–1042.
[12] C.-.Q. Jiang, L.-.T. Quan, F. Shi, N. Yang, C.-.H. Wang, X.-.M. Yin, Q.-.S. Zheng, Distribution of mineral nutrients and active ingredients in aloe vera irrigated with diluted seawater, Pedosphere 24 (2014) 722–730.
[13] S. Xin, M. Li, J. Shen, Effect of temperature and concentration ratio on pitting resistance of 316L stainless steel in seawater, Acta Metall. Sinica 50 (2014) 373–378.
[14] T. Higuchi, H. Fujimura, T. Arakaki, T. Oomori, The synergistic effects of hydrogen peroxide and elevated seawater temperature on the metabolic activity of the coral Galaxea fascicularis, Mar. Biol. 156 (2009) 589–596.
[15] R. Kovalenko, R.E. Melchers, B. Chernov, Long-term immersion corrosion of steel subject to large annual variations in seawater temperature and nutrient concentration, Struct. Infrastruct. Eng. 13 (2017) 978–987.
[16] Z. Razzaq, M.A.E. Dabbagh, M.B. Sirjani, R. Prabhakaran, Concrete Slabs Reinforced with FRP or Steel Reinforcements, J. Reinf. Plast. Compos. 28 (2009) 1111–1121.
[17] T. Qin, Y. Zhao, G. Lin, S. Hu, C. An, D. Geng, C. Rao, Underwater archaeological investigation using ground penetrating radar: a case analysis of Shanglinhu Yue Kiln sites (China), J. Appl. Geophys. 154 (2018) 11–19.
[18] X. Li, Y. Zhang, H. Feng, J. Guo, H. Li, Research current situation and development of polyurethane coatings, Appl. Chem. Ind. 39 (2010) 1091–1095.
[19] Y. Zhu, J. Xiong, Y. Tang, Y. Zuo, EIS study on failure process of two polyurethane composite coatings, Prog. Org. Coat. 69 (2010) 7–11.
[20] J.F. Huang, Y.T. Zhang, X.R. Zeng, L.Y. Cao, F. Deng, J.P. Wu, Hydrothermal etectrophoretic deposition of yttrium silicate coating on SiC-C/C composites, Mater. Technol. 22 (2007) 85–87.
[21] X.M. Song, G. Yu, H.B. Yi, L.Y. Ye, B.N. Hu, Phosphate-silicate composite coating formed on AM60 magnesium alloy, Surf. Eng. 26 (2010) 371–377.
[22] H.Y. She, B.E. Sleep, The effect of temperature on capillary pressure-saturation relationships for air-water and perchloroethylene-water systems, Water Resour Res 34 (1998) 2587–2597.
[23] M. Arjmandi, B. Tohidi, A. Danesh, A.C. Todd, Is subcooling the right driving force for testing low-dosage hydrate inhibitors? Chem. Eng. Sci. 60 (2005) 1313–1321.
[24] A.A. Watwe, A. BarCohen, A. McNeil, Combined pressure and subcooling effects on pool boiling from a PPGA chip package, J. Electron Packag. 119 (1997) 95–105.
[25] P.K. Kaushik, V.K. Varshney, P. Kumar, P. Bhatia, S.V. Shukla, Microwave-assisted synthesis, characterization, and antimicrobial activity of some odorant Schiff bases derived from naturally occurring carbonyl compounds and anthranilic acid, Synth. Commun. 46 (2016) 2053–2062.
[26] B. Davidde, Underwater archaeological parks: a new perspective and a challenge for conservation - The Italian panorama, Int. J. Naut. Archaeo. 31 (2002) 83–88.
[27] X. Wang, B. Zhang, Y. Hu, Research on extraction of fragile bamboo slips by underwater temporary solidification in original state, J. Cult. Herit. 51 (2021) 174–181.

Journal of Cultural Heritage 51 (2021) 174–181

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

Original article

Research on extraction of fragile bamboo slips by underwater temporary solidification in original state

Xinxin Wang[a], Bingjian Zhang[a,b,*], Yulan Hu[a]

[a] Department of Cultural Heritage and Museology, Zhejiang University, Hangzhou 310028, PR China
[b] Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 9 April 2021
Accepted 25 August 2021
Available online 16 September 2021

Keywords:
Underwater cultural relics
Waterlogged bamboo slips
Temporary solidification
Veratraldehyde

ABSTRACT

The complex preservation conditions make underwater cultural relics, especially organic ones—more fragile than terrestrial relics. Bamboo slips, the main carriers of ancient Chinese characters, are often found underwater. They have high cultural and historical values, but their mechanical strength is low, making them difficult to extract. Moreover, if their arrangement is disrupted during the extraction process, the subsequent restoration will be harder. In this study, veratraldehyde, a new underwater temporary solid material, was used to conduct in-situ reinforcement and extraction experiments on organic cultural relics. Based on these experiments, the researchers designed a three-layer wrapped protective frame and proposed the recovery method of dissolution and effective residue detection of nuclear magnetic resonance (NMR). The experimental results showed that this method can nearly preserve the original state of fragile bamboo slips underwater and extract them out of the water safely. Also, the solidification process is reversible and without residues. It is a safe and reliable underwater technology for solidifying extraction of cultural relics.

© 2021 Elsevier Masson SAS. All rights reserved.

1. Introduction and research aim

In 2001, the United Nations Educational, Scientific and Cultural Organization (UNESCO) in Paris, France, proposed the "Convention on the Protection of Underwater Cultural Heritage [1]." The convention pointed out that underwater cultural heritage includes all the remains and traces of life that are underwater life related to ancient people, including architectural ruins, handicrafts, aircraft wreckage, sunken ships and their cargo, and relics of prehistoric significance [2]. Unlike land-based cultural relics, underwater cultural relics have been immersed in water for a long time and some of them are buried by silt or sand. The oxygen-free environment has preserved these cultural relics so that they are closer to their original appearance than land-based relics [3]. However, the complex chemical environment in the water will still reduce the mechanical strength of these cultural relics. If protective measures are not taken as soon as possible, the world's cultural heritage and its diversity will experience a major loss [4,5].

Bamboo slips are the main media for writing documents in China before the widespread introduction of paper during the first two centuries AD [6]. "It is woven with hemp rope, like a bamboo curtain, which can be unrolled [7]." Bamboo slips record a large amount of political, economic, legal, and literary information, which has great historical and archeological value. Department of Chinese, Sun Yat-sen University indicated that bamboo slips have appeared during the Shang and Zhou dynasties [8]. The earliest archeological evidence of bamboo slips discovered is Zeng slips in the early Warring States period and Xinyang Chu slips, dated to around 400 BC in China [9,10]. The latest bamboo slips are Wu Slips in Changsha Zoumalou, respectively, in AD 369 and 237 [11,12].

Among the bamboo slips discovered so far, many have been found in wells and tombs underwater [13,14]. Because the hemp rope rots and the bamboo slips are fragile, it is extremely difficult to preserve coherently from their original archeological context [15]. Once the bamboo slips are out of order, reading the written information on them is very difficult [16].

The current method used for the extraction of fragile land-based cultural relics is generally temporary solidification. Foreign objects can be temporarily wrapped and removed, using the supporting force of the phase change of the material surrounding the artefact from liquid to solid to give the fragile body sufficient mechanical strength to allow safe removal. Cyclododecane and menthol that can be removed by sublimation, are primarily used to reinforce unearthed relics temporarily and ensure their safe transfer [17–19]. However, due to the density or solubility, these materials cannot be applied to underwater cultural relics.

* Corresponding author.
E-mail address: zhangbiji@zju.edu.cn (B. Zhang).

https://doi.org/10.1016/j.culher.2021.08.008
1296-2074/© 2021 Elsevier Masson SAS. All rights reserved.

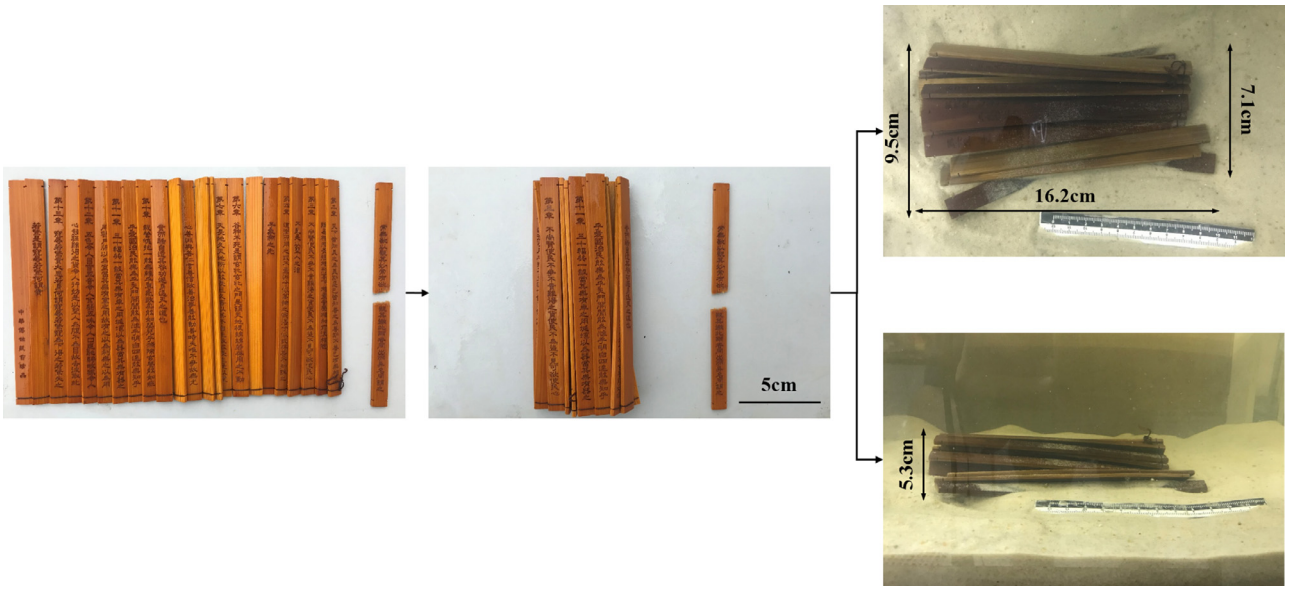

Fig. 1. Bamboo-slip pretreatment process.



Fig. 2. Fabric for square frame for extraction.

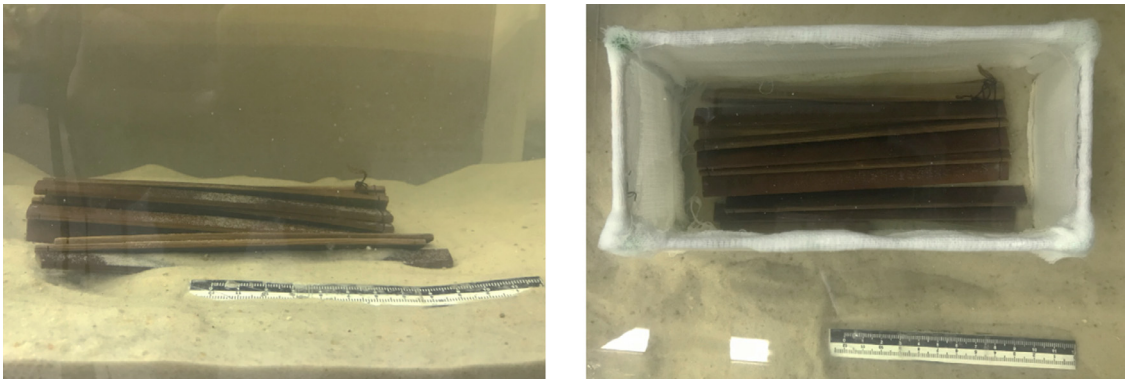

Fig. 3. Bamboo slips and frame under water.

The Survey, Assess, stabilise, Monitor And Preserve underwater archeological sites organization (SASMAP) has conducted detailed experiments on the following methods: gauze-wrapping method, carbon-fiber reinforced epoxy-resin method, and liquid-nitrogen reinforcement method [20]. Among them, the first two methods need to move cultural relics during the operation. However, for the extraction of a large number of bamboo slips, it is very important to keep the bamboo slips in their original state, so the first two methods are not applicable. The liquid-nitrogen reinforcement method enables extraction without disturbance well, but it is not known whether the instantaneous thermal changes damage the bamboo slips of this type of internally decayed cultural relics.

Considering the difficulty of the solidification and extraction of fragile bamboo slips underwater, we optimized the entire salvage process based on previous research [21,22], including the use of veratraldehyde (3,4-dimethoxybenzaldehyde) for primary reinforcement, epoxy-resin adsorbed polyurethane sponge for secondary reinforcement and adhesive bandages for tertiary reinforcement [23]. Also, we optimized the method of solidification and the complete removal of the temporary-solidification material, so that

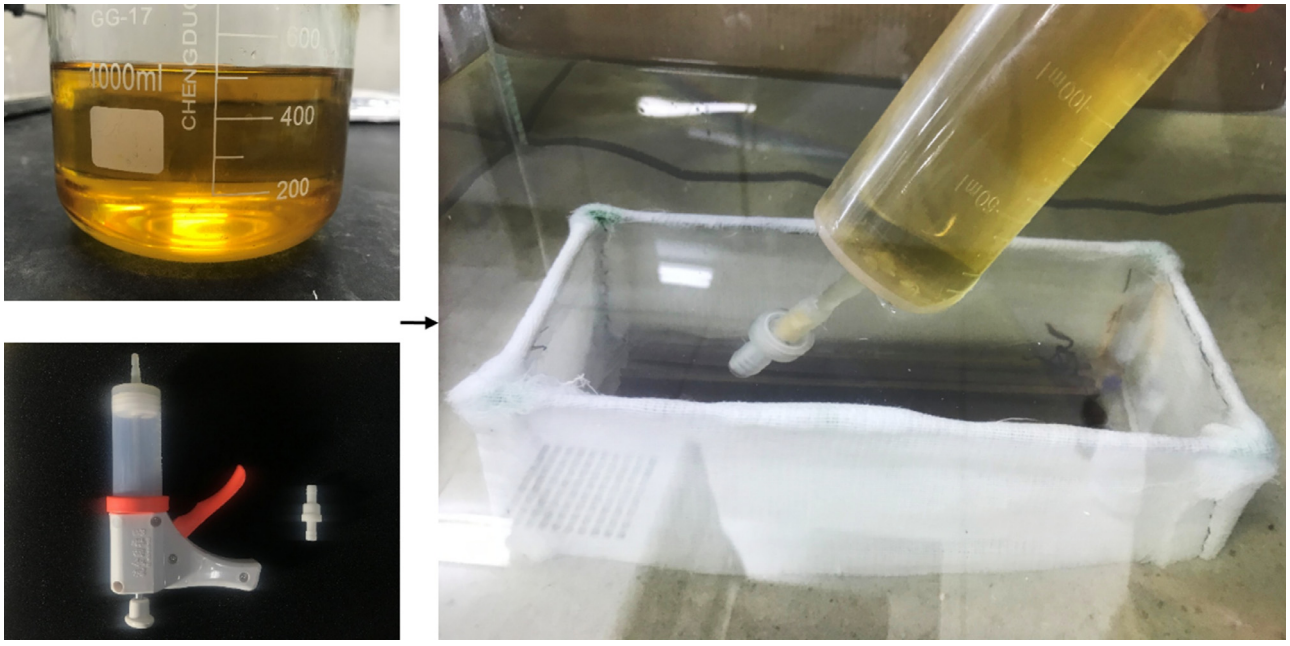

Fig. 4. Add veratraldehyde to solidify in-situ underwater.

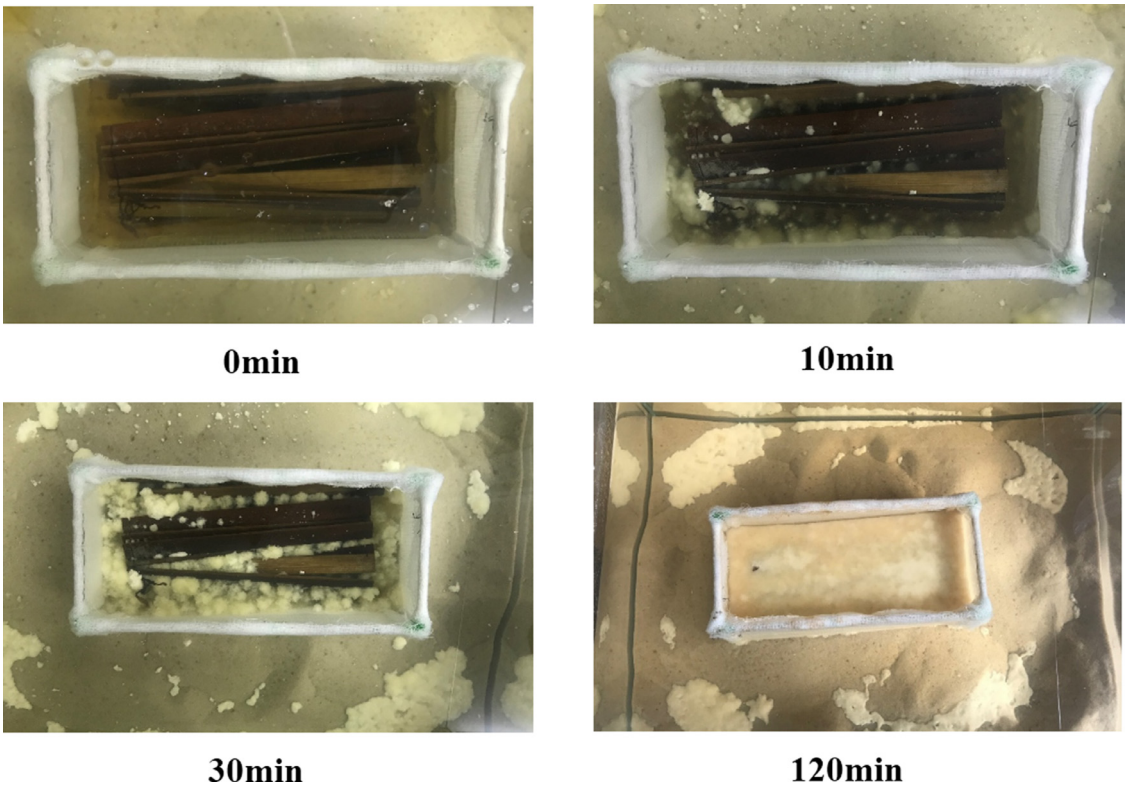

Fig. 5. Underwater solidification of Veratraldehyde.

the bamboo slips could be displayed in the exhibition hall in their original underwater state.

2. Materials and methods

Veratraldehyde is also known as “methyl vanillin” and its chemical name is “3,4-dimethoxybenzaldehyde.” It is an important synthetic spice and pharmaceutical intermediate [24]. Harmful if swallowed and mildly irritating to eyes, respiratory system, and skin. Because of its safety and suitable physical properties, it can be applied to the salvage and extraction of underwater cultural relics. The main reasons that veratraldehyde can be used in this field are as follows: (1) The pH value of veratraldehyde is neutral and will not corrode the cultural relics. (2) Veratraldehyde has a low melting point of approximately 40–43 °C and is only slightly soluble in hot water. These characteristics make it suitable for reinforcing artefact in outdoor environments. (3) Under normal temperature conditions, liquid veratraldehyde can maintain a molten state for

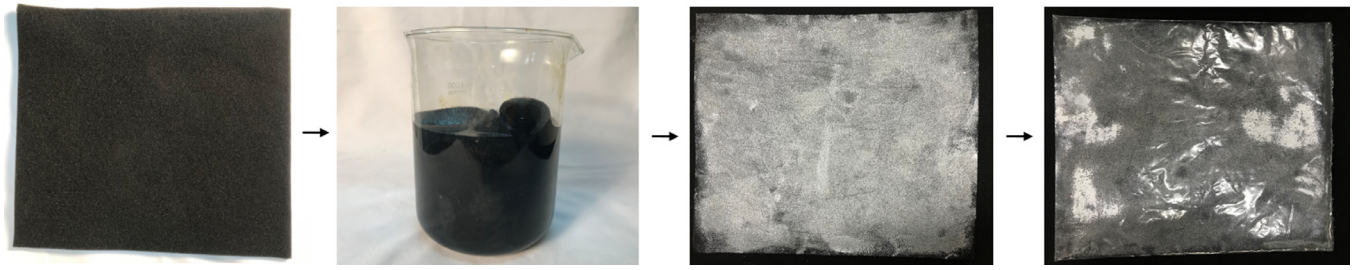

Fig. 6. Process for the preparation of the second protective layer.

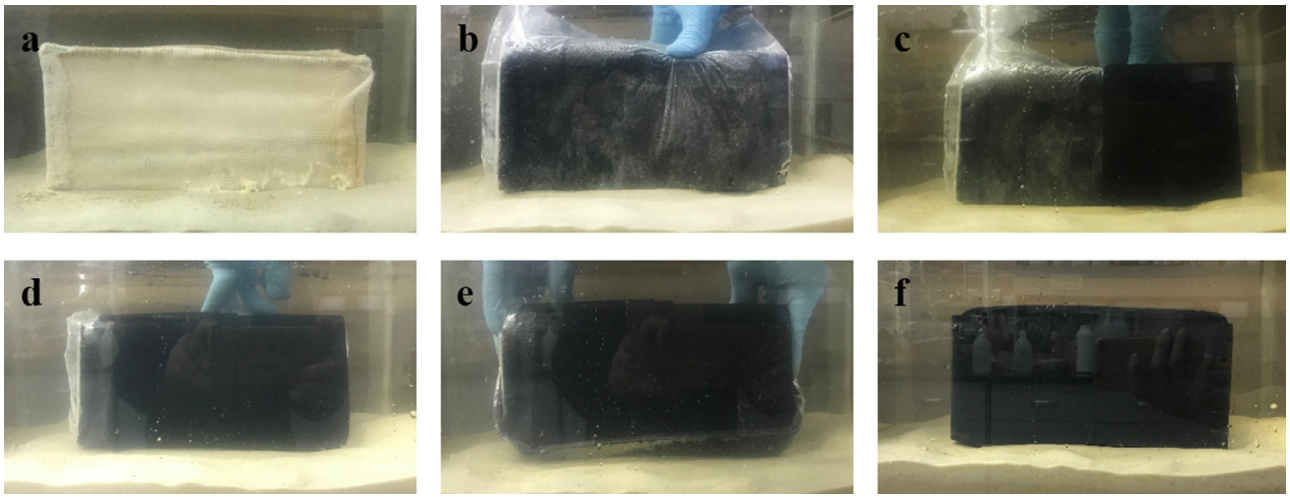

Fig. 7. Underwater packing and extraction process
(a) Front view of underwater frame; (b) use polyurethane sponge-epoxy to wrap the frame; (c) wrap with self-adhesive bandage; (d) Repeat Step c; (e) wrap the frame side; (f) wait for the epoxy to cure.

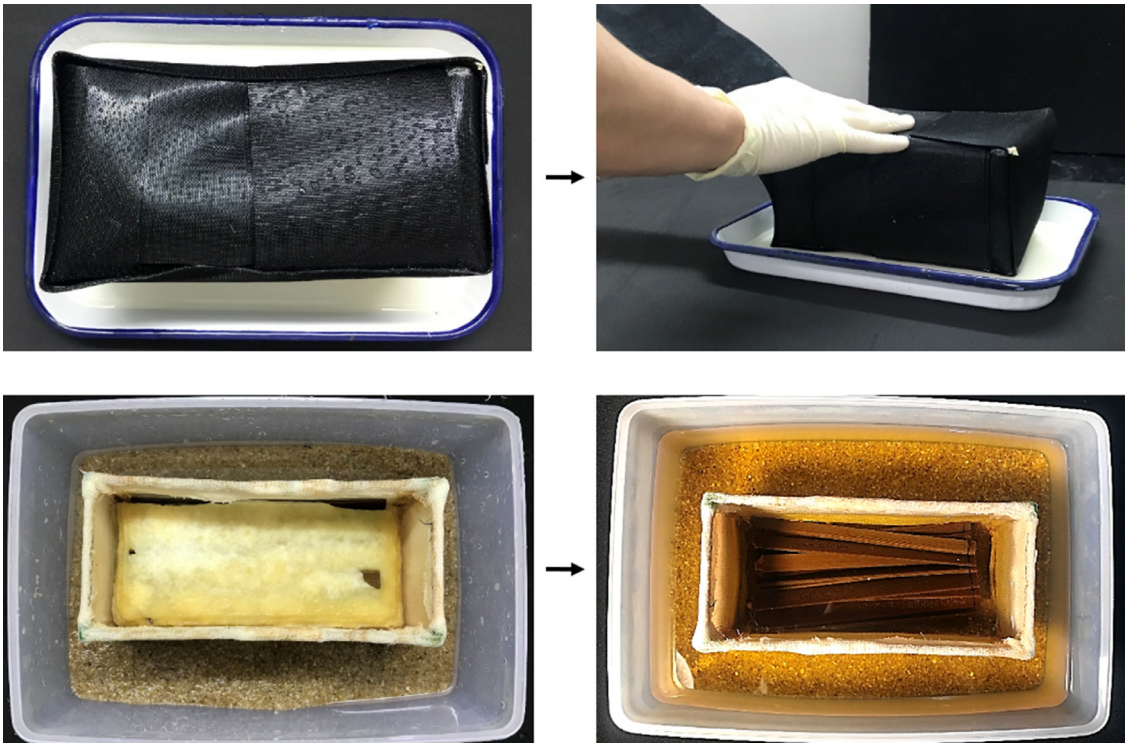

Fig. 8. Dissolution process.

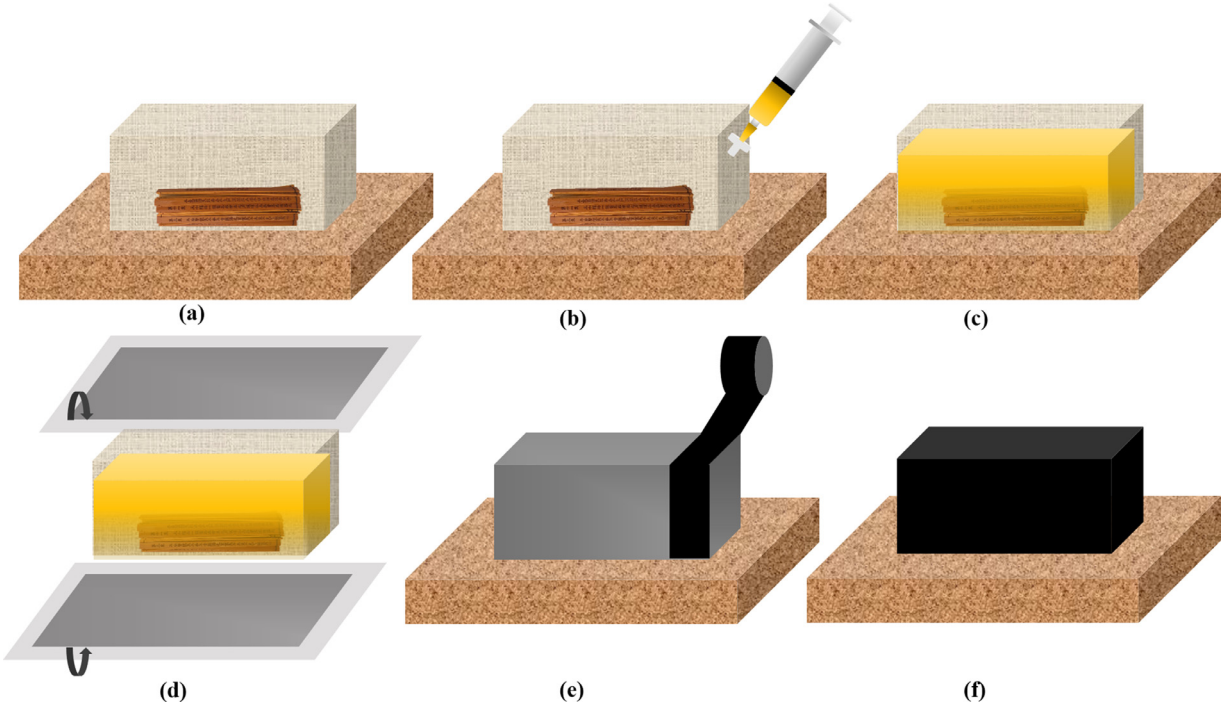

Fig. 9. Operation process of the solidifying extraction process
(a) Place the underwater bamboo slips in the extraction frame; (b) inject veratraldehyde into the frame; (c) wait for the veratraldehyde to completely solidify; (d) use the polyurethane sponge that absorbs epoxy resin to wrap the frame as a whole; (e) use a self-adhesive bandage to wrap the epoxy-sponge; (f) complete in-situ solidifying extraction.

more than 10 min [25], leaving time for actual operations in the underwater environment.

In this experiment, we used veratraldehyde (Macklin, 99%) for temporary reinforcement. The objects are samples of degraded processed bamboo slips, furthermore, the scanning electron microscope (SEM) was used to observe the deterioration of the cell wall and evaluate the method of removing the protective layer. In order to detect the residues on the bamboo slips after extraction, we performed Bruker AVANCE III (400 MHz) to determine whether the expected zero-residue effect was achieved.

2.1. Preparation and pretreatment of bamboo slips

Underwater, bacteria degrade the cellulose, hemicellulose, and lignin contained in the cell wall of the bamboo of the slips, destroying the mechanical structure [26]. At the same time, the rope used for binding also decays. Therefore, the overall state of the bamboo slips is very fragile. In order to simulate this state, we cut off the rope on one side of the bamboo slips, and took one of the bamboo pieces and folded it into two sections to show the possible conditions under extreme damage. The aging and waterlogging were completed by letting the pieces of folded bamboo heat and react to 2.5 M NaOH solution at 60 °C for one week [27]. After washing them, we put them underwater. The ion concentration of water was equal to that of seawater (35 *wt*‰ NaCl), and the bottom was covered with sand to simulate a real underwater environment.

The dimensions of the bamboo slips underwater were 16.2 cm long, 9.5 cm wide on the left, and 7.1 cm wide on the right and that the exposed part of the sand layer was 5.3 cm high Fig. 1.

2.2. Making the frame

The purpose of making the frame is twofold: Firstly, to confine the flow of the molten veratraldehyde and to affect the solidification process. The other is to increase the overall support strength, which is convenient for underwater operation and salvage.

We designed and made a metal cuboid frame with a length of 21.0 cm, a width of 10.0 cm, and a height of 10.0 cm. Then, two layers of medical gauze were used to wrap and fix the frame, and the contact surface was treated with waterproof glue (Acrylic AB glue, KSIMI, China), as shown in Fig. 2.

Before putting the frame into the water, we used a soft brush to remove the sand on the bamboo slips' surface. If the amount of sand was large, we first used a sand-suction device to take away the surface sand. Second, the frame was placed into the water. Third, the frame completely covered the bamboo slips. In order to make the frame fit close to the bottom surface, it needed to be pressed a heavy object down for a period of time to ensure that the veratraldehyde would not leak out from below when it was solidifying *in-situ* Fig. 3.

2.3. Solidification on site

According to calculations, we weighed 1 kg of veratraldehyde, heated it to a liquid state at 60 °C, poured it into a syringe equipped with a one-way valve, and then slowly injected it into the frame before solidified Fig. 4.

We injected veratraldehyde into the frame in stages until the bamboo slips were completely covered and made a solidified mass of bamboo slips, veratraldehyde, and frame, as shown in Fig. 5.

2.4. Packing and extraction

To prevent damage to the bamboo slips-veratraldehyde-frame structure due to insufficient strength during extraction from water, we designed a second protective layer: a high-strength layer comprising polyurethane sponge filled with epoxy resin (E51: JH593 = 2:1, Jinhong Rubber Industry, China) Fig. 6.

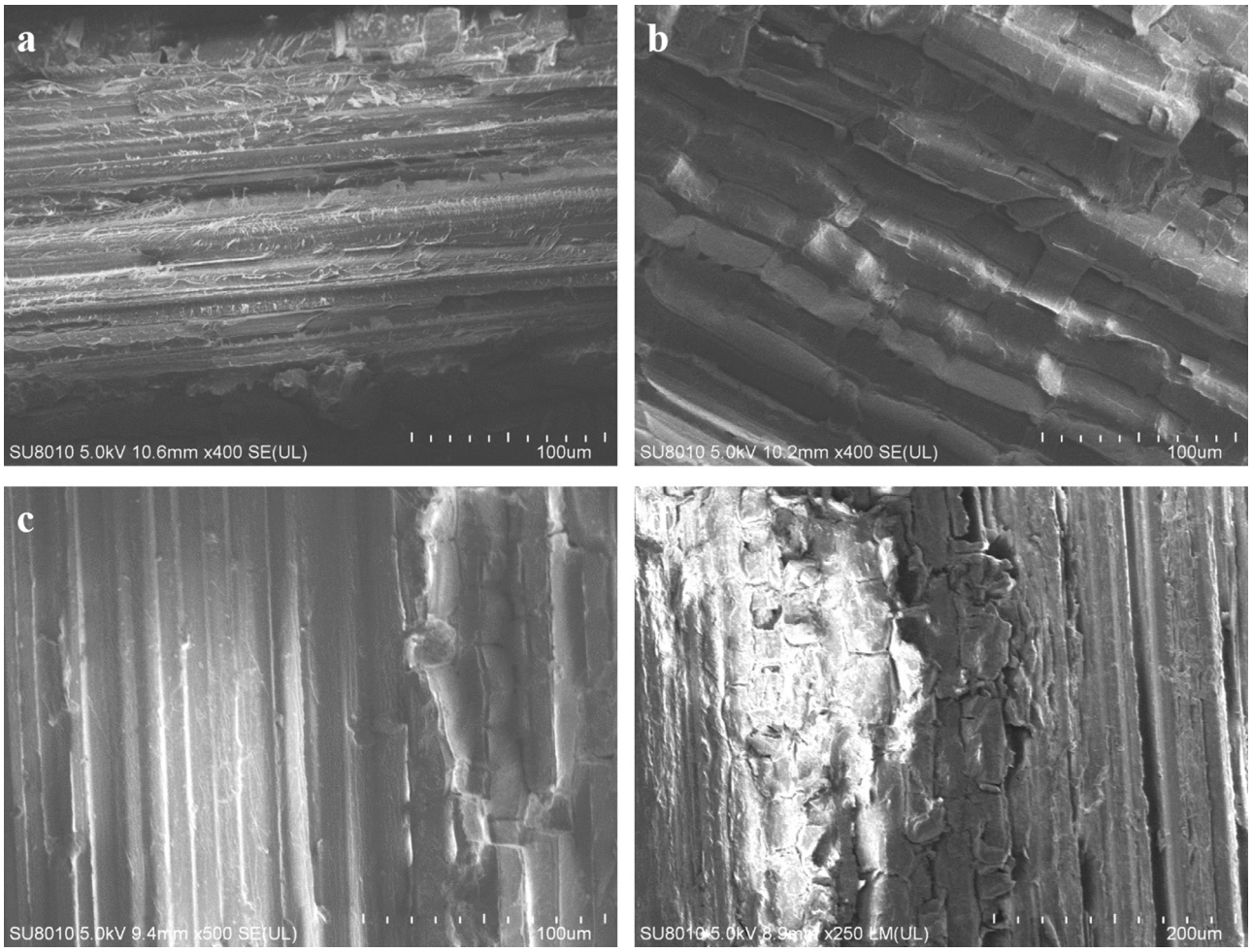

Fig. 10. SEM of the bamboo slips (a: fresh bamboo slips, b: NaOH solution soaked bamboo slips, c: sample after removal of dissolution, d:sample after removal of sublimation).

We used porous polyurethane sponge instead of traditional carbon-fiber cloth. This adjustment was because the sponge had a certain thickness (0.5 cm) that can effectively cushion the impact of possible collisions on internal materials. At the same time, polyurethane sponge is a loose, porous material that can quickly and massively absorb epoxy resin, eliminating the time needed for the underwater reaction.

Next, we cut two sponges according to the size of the frame (40 × 20 × 0.5 cm, 40 × 10 × 0.5 cm), cleaned with ethanol, mixed a sufficient amount of epoxy resin, according to the manufacturer's instructions, and quickly applied it to the sponge material. We put them into a vacuum bag, expressed the air from the bag, and then put it underwater for wrapping. Finally, the third layer was wrapped and fixed with a self-adhesive bandage on the outermost layer. The specific process is shown in Fig. 7.

2.5. Return to the original state

The bamboo slips that are protected by the three layers of wrapping have strong anti-deformation capacity. After removing the protected slips from the water and transporting them to a water tank, we removed the protective layers one at a time. For temporary solidification materials such as veratraldehyde, there are currently two commonly used removal methods:

(1) *Sublimation method*. Because of characteristics with high saturated vapor pressure, veratraldehyde would be completely volatilized in a blast-drying box at a certain temperature, to achieve zero residues.
(2) *Dissolution method*. The low concentration of ethanol solution completely dissolves the veratraldehyde, and will not damage bamboo slips.

We studied the solubility of veratraldehyde in ethanol solutions of different concentrations(0–30%) and found that 20% ethanol solution at 25 °C has a more suitable dissolving effect in ensuring the safety of the cultural relics [22]. After about a week of soaking, the veratraldehyde should be completely dissolved, and the original arrangement of the bamboo slips under the water should be completely preserved Fig. 8.

Due to the potential damage to the bamboo slips during the drying process at high temperatures and the fact that veratraldehyde itself is readily soluble in ethanol solution, we preferred the solvent dissolution method. Meanwhile, we used SEM to examine bamboo slips from both the sublimation and solution.

Samples for the sublimation method were placed in a blast-drying box at 30 °C for one week until the mass no longer changes. For the dissolution method, the samples are freeze-dried in the freezer dryer (FD5–2.5, SIM, USA) after the protective layer complete dissolution. The cell wall degradation after gold coating was examined with a field emission scanning electron microscope, which was operated at an operating voltage of 5.0 kV for SEM observations.

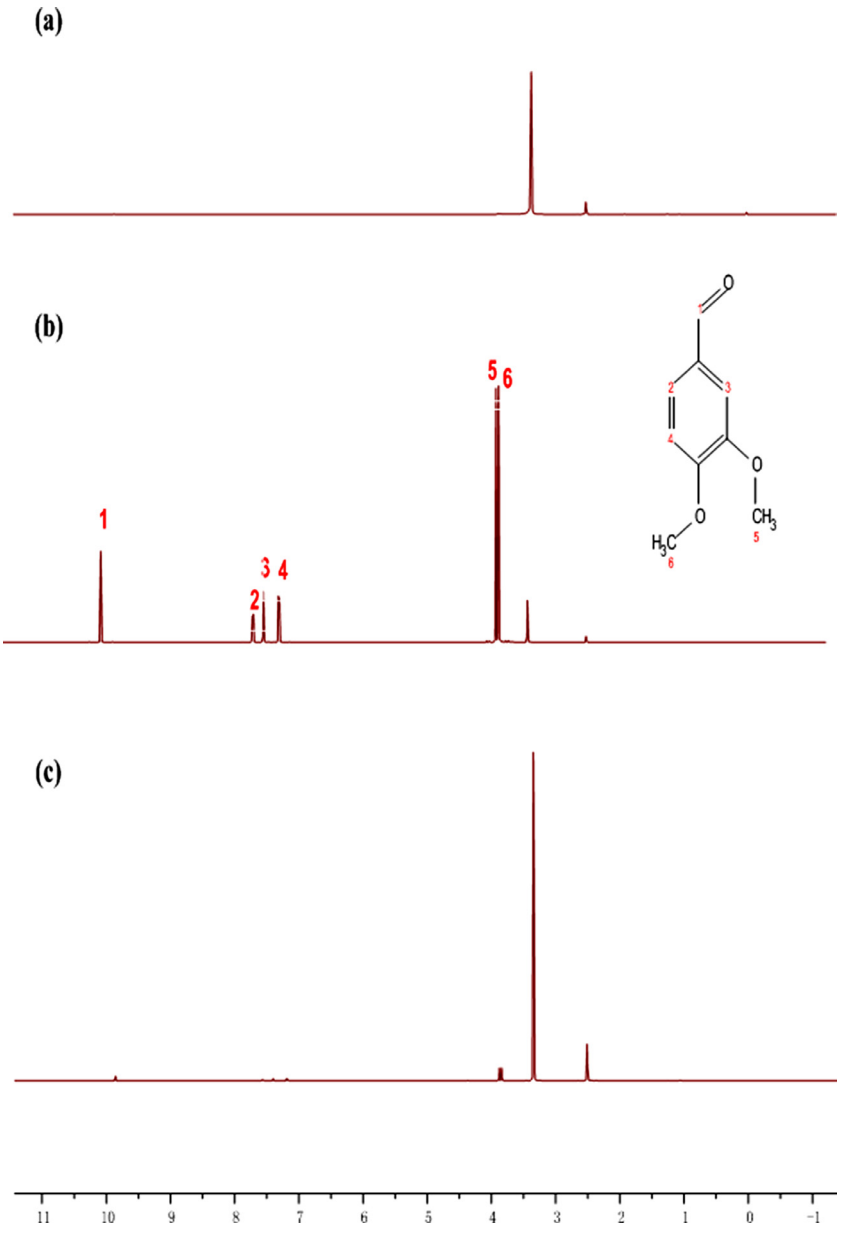

Fig. 11. Comparison chart of residue ^{1}H NMR analysis
(a) original bamboo slips; (b) pure sample of veratraldehyde; (c) extracted bamboo slips.

2.6. Residue detection

The advantages of veratraldehyde as a temporarily solid material are rapid reinforcement, easy removal, and lack of residue. In order to verify whether veratraldehyde or its oxidation products remain in the bamboo slips, we carried out a ^{1}H NMR test with TMS as internal standard on the extracted bamboo slips, the original bamboo slips (Not reinforced with veratraldehyde), and the pure sample of veratraldehyde. The researchers dried the three samples at a constant temperature of 80 °C for 24 h, weighed out 10 mg separately, and treated the material with 0.5 ml DMSO-d6 before analysis.

3. Results

3.1. Extraction process

According to this method, veratraldehyde is used to temporarily solidify bamboo slips. The process of this method is summarized in Fig. 9. During restoration and display, the original arrangement of bamboo slips under water should be completely unchanged and ensure there will be no residues of materials that may damage the cultural relics, indicating that this method is feasible for extracting fragile slips and solidifying them in their original state.

3.2. SEM of the sample after removal of the methods

After using the two methods to remove the protective layer, we evaluated both methods using SEM and added fresh and NaOH solution soaked bamboo slips for comparison, as shown in Fig. 10.

The cell walls of fresh bamboo slips were dense, and those soaked in NaOH solution showed some degree of wrinkling, indicating that the degradation to the bamboo slips was effective. The bamboo slips obtained using the dissolution method did not differ much from those in b, but those obtained using the sublimation method showed severe peeling and wrinkling of the cell walls.

3.3. Residue analysis

We carried out ^{1}HNMR analysis to determine whether veratraldehyde and its oxidation products remained in the bamboo slips. The analysis results are shown in Fig. 11.

It shows that the original bamboo slips only showed the solvent peak of water. In pure veratraldehyde, there are three hydrogen peaks at chemical shift values 7.57, 7.39, and 7.18 ppm, indicating three other hydrogens on the benzene ring. Chemical shift at 9.84 ppm refers to the hydrogen on the aldehyde group. The sharp peaks at 8.87 and 8.83 ppm are attributed to the two methoxys, and the value 2.5 ppm represents the solvent peak of DMSO-d6.

The extracted bamboo slips also showed hydrogen peaks on the benzene ring at chemical shift values of 3.87 and 3.83, which showed that veratraldehyde was present, but its concentration was lower than 2 mM, and it could be completely volatilized during future preservation due to its own high saturated vapor pressure.

4. Conclusion

This article described a novel application of veratraldehyde, a temporary solid material for underwater in-situ solidifying-extraction, for a simulation experiment on underwater bamboo slips. We designed a three-layer package structure that effectively solved the problem of safe extraction of saturated bamboo slips in situ. At the same time, it was found that the removal of the protective layer by the sublimation method would cause serious damage to the structure of the bamboo slips, while the dissolution method would not. In addition, through the detection of residues on the bamboo slips, we found that with this method there are limited residual amounts of vertraldehyde after lifting and extracting in ethanol and that the veratraldehyde will continue to volatilize in the future display process and eventually achieve the condition of zero residues.

Acknowledgements

National key R&D Program of China (2020YFC1521804) is greatly acknowledged for their financial support.

References

[1] U. Koschtial, The 2001 UNESCO convention on the protection of the underwater cultural heritage: advantages and challenges, in: Museum International, 60, 2008, pp. 63–69.
[2] UNESCO, Convention on the protection of the underwater cultural heritage, in, 2001.
[3] J. Liao, H. Fukui, T. Urakami, H. Morisaki, Effect of biofilm on ennoblement and localized corrosion of stainless steel in fresh dam-water, Corros. Sci. 52 (2010) 1393–1403.
[4] C. Remazeilles, M. Saheb, D. Neff, E. Guilminot, K. Tran, J.-.A. Bourdoiseau, R. Sabot, M. Jeannin, H. Matthiesen, P. Dillmann, P. Refait, Microbiologically influenced corrosion of archaeological artefacts: characterisation of iron(II) sulfides by Raman spectroscopy, J. Raman Spectrosc. 41 (2010) 1425–1433.
[5] F. Antonelli, C.S. Perasso, S. Ricci, B.D. Petriaggi, Impact of the sipunculan Aspidosiphon muelleri Diesing, 1851 on calcareous underwater cultural heritage, Int. Biodeterior. Biodegrad. 100 (2015) 133–139.
[6] W. Chengxue, Early Chinese characters and stylistic concepts, Lit. Rev. 06 (2016) 14–24.
[7] Z. Xiancheng, General Theory of Bamboo and Silk Philology, Zhong Hua Book Company, Beijing, 2004.
[8] S.Y. SU, Department of Chinese, An overview of chu bamboo slips during the warring states period, J. Sun Yat-Sen Univ. (1978) 62–71 Social Science Edition.
[9] H.P. Museum, Tomb of Marquis Yi of Zeng, Cultural Relics Publishing House, Beijing, 1989.
[10] H.P.I.O.C. Relics, Xinyang Chu Tomb, Cultural Relics Publishing House, Beijing, 1986.
[11] L. Chai, Y. Chen, Y. Huang, Z. Yang, Diversity of culturable microorganisms from erosive bamboo slips of kingdom Wu, J. Cent. South Univ. Sci. Technol. 41 (2010) 1674–1679.
[12] L. Xiaoguang, Textual research on bamboo based on bamboo slips, J. Bamboo Res. 37 (2018) 1–6.
[13] L. Guan, Indoor cleaning and protection of bamboo slips unearthed from the tomb of the Hou Liu He in the western Han dynasty, Cultural Relics 06 (2020) 17–24 +40.
[14] P. Huang, A brief report on the excavation of bamboo slips from the eastern Han dynasty at Wuyi square in Changsha Hunan, in: Cultural Relics, 06, 2013, pp. 4–26. +21-22.
[15] G. Zhao, Introduction to protection of bamboo slips, China Cultur. Herit. Sci. Res. 02 (2006) 59–67.
[16] L. Li, On-site protection of cultural relics unearthed from the Tomb of Chu in the warring states period in Jiangling Area–Preservation of lacquered wood and bamboo slips, Archaeol. Cult. Relics 06 (2000) 72–79.
[17] H. Luo, X. Han, X. Huang, W. Li, Progress in uses of cyclododecane in art conservation, Mater. China 31 (2012) 48–55.
[18] X. Han, B. Rong, X. Huang, T. Zhou, H. Luo, C. Wang, The use of menthol as temporary consolidant in the excavation of Qin Shihuang's terracotta army, Archaeometry 56 (2014) 1041–1053.
[19] X. Han, X. Huang, B.J. Zhang, Laboratory research into the use of menthol as a temporary consolidant for conservation on archaeological excavations, Archaeometry 60 (2018) 1334–1345.
[20] B.D. Petriaggi, D.J. Gregory, J. Dencker, Recovery of fragile objects from underwater archaeological excavations: new materials and techniques by SASMAP project, in: M. Ioannides, N. MagnenatThalmann, E. Fink, R. Zarnic, A.Y. Yen, E. Quak (Eds.), Digital Heritage: Progress in Cultural Heritage, Documentation, Preservation, and Protection, 2014, pp. 625–634.
[21] X.Q. Chen, L. Xie, F. Wang, Y. Wu, B. Zhang, L. Zhu, Temporary consolidation and packaging of fragile cultural relics at underwater archaeological sites to maintain their original state during extraction, Archaeometry 62 (2020) 1067–1077.
[22] F. Wang, X. Chen, X. Wang, B. Zhang, Y. Hu, L. Zhu, Technique of temporary undisturbed reinforcement extraction of fragile Lacquerware from shipwrecks, J. Marit. Archaeol. 16 (2021) 27–38.
[23] T. Wang, D. Xiong, T. Zhou, Preparation and wear behavior of carbon/epoxy resin composites with an interpenetrating network structure derived from natural sponge, Carbon NY 48 (2010) 2435–2441.
[24] M. Melian-Rodriguez, S. Saravanamurugan, S. Kegnaes, A. Riisager, Aerobic oxidation of veratryl alcohol to veratraldehyde with heterogeneous ruthenium catalysts, Top. Catal. 58 (2015) 1036–1042.
[25] X.Q. Chen, B. Zhang, Z. Zhang, Application of veratraldehyde as a temporary consolidant for relics at underwater cultural heritage sites, Archaeometry 61 (2019) 1417–1429.
[26] Z. Liu, T. Fu, C. Hu, D. Shen, N. Macchioni, L. Sozzi, Y. Chen, J. Liu, X. Tian, Q. Ge, Z. Feng, H. Liu, Z. Zhang, J. Pan, Microbial community analysis and biodeterioration of waterlogged archaeological wood from the Nanhai No. 1 shipwreck during storage, Sci. Rep. 8 (2018).
[27] B. Godin, R. Agneessens, S. Gofflot, S. Lamaudiere, G. Sinnaeve, P.A. Gerin, J. Delcarte, Review on analytical methods for lignocellulosic biomass structural polysaccharides, Biotechnol. Agron. Soc. Et Environn. 15 (2011) 165–182.

证书号第4789067号

发明专利证书

发明名称：一种水下脆弱文物原位固型多重包裹的提取材料和提取复原方法

发明人：张秉坚;陈学强;王新鑫

专利号：ZL 2021 1 0157108.1

专利申请日：2021年02月04日

专利权人：浙江大学

地址：310058 浙江省杭州市西湖区余杭塘路866号

授权公告日：2021年11月12日　　授权公告号：CN 112812544 B

国家知识产权局依照中华人民共和国专利法进行审查，决定授予专利权，颁发发明专利证书并在专利登记簿上予以登记。专利权自授权公告之日起生效。专利权期限为二十年，自申请日起算。

专利证书记载专利权登记时的法律状况。专利权的转移、质押、无效、终止、恢复和专利权人的姓名或名称、国籍、地址变更等事项记载在专利登记簿上。

局长
申长雨

国家知识产权局

2021年11月12日

其他事项参见续页

Rijksdienst voor Ondernemend Nederland

> Retouradres Postbus 10366 2501 HJ Den Haag

ir. M.B. Plaggenborg
Octrooibureau Novopatent
Picassoweg 38
1328 KN Almere
Nederland

Octrooicentrum Nederland, onderdeel van Rijksdienst voor Ondernemend Nederland
Octrooien, Valorisatie en Sectoren

Prinses Beatrixlaan 2
2595 AL Den Haag
Postbus 10366
2501 HJ Den Haag
www.rvo.nl/octrooien

ING Bank
IBAN: NL41INGB0705001296
BIC/Swift: INGBNL2A

Contactpersoon
Team Verlening
T (088) 042 63 33
teamverlening@rvo.nl

Onze referentie
ORE/2030700/L003

Uw referentie
P1101/NL

Datum 22/06/2023
Betreft Verlening van octrooi

Octrooi(aanvraag) 2030700
ten name van:
Zhejiang University te Hangzhou City, China

Geachte lezer,

Op bovengenoemde aanvraag is op 22/06/2023 onder nummer 2030700 octrooi verleend. Octrooicentrum Nederland zal de bij de aanvraag behorende beschrijving en tekeningen bij wege van octrooischrift uitgeven en u hiervan een gewaarmerkt afschrift, een zogenaamd octrooibewijs, verstrekken.

Het octrooi blijft, behoudens eerder verval of vernietiging door de rechter, van kracht tot het verstrijken van een termijn van 20 jaren gerekend vanaf de datum van indiening van de aanvraag, derhalve tot en met 24/01/2042.

Om het octrooi in stand te houden dient, voor het eerst vanaf het 4e jaar*, een jaartaks te worden betaald. Deze jaartaks dient voor de eerste keer te zijn voldaan op 31/01/2025 en is hierna jaarlijks op 31/01 verschuldigd. Raadpleeg het octrooiregister voor meer informatie over de door u verschuldigde taksen. Octrooicentrum Nederland stuurt hier geen rekening voor.

Betaling van de jaartaks is de verantwoordelijkheid van de octrooihouder.

* te rekenen vanaf datum indiening van de aanvraag of, indien sprake is van een afgesplitste aanvraag, de indieningsdatum van de oorspronkelijke aanvraag.

Na afloop van de betaaltermijn is het gedurende zes maanden mogelijk om de jaartaks met een verhoging van 50% te betalen. Wanneer ook na deze zes maanden geen betaling is ontvangen, vervalt het octrooi. In de bijlage vindt u de bedragen van de jaartaksen (zonder verhoging).

Met vriendelijke groet,

De directeur van Octrooicentrum Nederland,
namens deze:
Christa Swuste
medewerker team Octrooiregister

Dit bericht is automatisch gegenereerd en bevat daarom geen handtekening.

Octrooicentrum Nederland, onderdeel van Rijksdienst voor Ondernemend Nederland

Datum
22/06/2023

Onze referentie
ORE/2030700/L003

Bijlage bij Verlening van octrooi

Onderwerp: Jaartaksen

Hieronder vindt u de bedragen van de jaartaksen zoals vastgesteld in het Uitvoeringsbesluit Rijksoctrooiwet 1995. Betaling van de onderstaande jaartaksen dient te geschieden op de laatste dag van de maand waarin de aanvraag is ingediend (de vervaldag).
Betaling na de vervaldag is slechts mogelijk met verhoging van 50% van het voor dat jaar te betalen bedrag tot uiterlijk 6 maanden nadien.
Indien de verschuldigde jaartaks (eventueel vermeerderd met de verhoging) uiterlijk zes maanden na de vervaldag niet is voldaan, vervalt het octrooi.

Meer informatie over jaartaksen vindt u op de website op:
https://www.rvo.nl/onderwerpen/innovatief-ondernemen/octrooien-ofwel-patenten/octrooi-merk-model/octrooirecht/tarievenoverzicht

het eerste jaar	EUR	--,--
het tweede jaar	EUR	--,--
het derde jaar	EUR	--,--
het vierde jaar	EUR	40,--
het vijfde jaar	EUR	100,--
het zesde jaar	EUR	160,--
het zevende jaar	EUR	220,--
het achtste jaar	EUR	280,--
het negende jaar	EUR	340,--
het tiende jaar	EUR	400,--
het elfde jaar	EUR	500,--
het twaalfde jaar	EUR	600,--
het dertiende jaar	EUR	700,--
het veertiende jaar	EUR	800,--
het vijftiende jaar	EUR	900,--
het zestiende jaar	EUR	1.000,--
het zeventiende jaar	EUR	1.100,--
het achttiende jaar	EUR	1.200,--
het negentiende jaar	EUR	1.300,--
het twintigste jaar	EUR	1.400,--

Overzicht geregistreerde gegevens bij verlening

Octrooinummer	: 2030700	**Ingediend**:	25/01/2022	
IPC	: B63C 7/00, B65D 81/02, B65B 23/00, C08J 9/36			
Recht van Voorrang	: 202110157108.1	04/02/2021	China	
Datum inschrijving	: 08/09/2022			
Verleningsdatum	: 22/06/2023			
Maximale duur	: 24/01/2042			
Verzoek vervroegde inschrijving	:	**Ingediend:**		
Vno soort	: Nieuwheidsonderzoek-Nationaal	**Ingediend:**	25/01/2022	
Gewijzigde stukken	: Nee			
Korte aanduiding	: IN-SITU REINFORCEMENT MULTI-WRAPPED EXTRACTION MATERIAL AND EXTRACTION AND RESTORATION METHOD FOR UNDERWATER FRAGILE CULTURAL RELICS			
Tenaamstelling	: Zhejiang University te Hangzhou City, China			

Houder(s) :
Zhejiang University
866 Yuhangtang Road
Xihu District
Zhejiang
310058 Hangzhou City
China

Uitvinder(s) :
Bingjian Zhang
Hangzhou City
China

Xueqiang Chen
Hangzhou City
China

Xinxin Wang
Hangzhou City
China



Gemachtigde : ir. M.B. Plaggenborg
Octrooibureau Novopatent
Picassoweg 38
1328 KN Almere
Nederland