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Scientific investigation of the paint and adhesive materials used in the Western Han dynasty polychromy terracotta army, Qingzhou, China

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ABSTRACT

A royal tomb of early period of the Western Han dynasty (206 B.C–8 A.D) was excavated by archaeologists in Qingzhou County, Shandong Province in 2006. Over 2000 polychromy terracotta soldiers, horses, chariots, servants etc. were unearthed from the tomb. All the terracotta figures are one quarter or one sixth as large as the livings, most of them were painted with well designed patterns. In order to gain complete information about the materials and techniques used for the polychromy on the terracotta army, five samples from the painted areas were taken. In addition, one sample from the area to adhere one leg to the ploychromy horse body was also obtained. The analytical techniques applied include XRF, FTIR, Py-GC/MS and GC/MS. Chinese purple, cinnabar, lead red and ochre were used as pigments, while animal glue was identified as binding medium and adhesive in the polychromy terracotta army in the Han Dynasty. The results definitely will provide new evidence about the materials and technologies used in Han Dynasty. Especially, the binding medium identified is different in comparison with Qin Shihuang's terracotta army (259–210 BC).

1. Introduction

A Han dynasty royal tomb was excavated in Xiangshan, Qingzhou county, Shandong province, China in 2006. The tomb pit is about 7.3 m long (south to north) and 5.1 m wide (east to west). It dates back to early Western Han period (206–8 AD). About 2000 polychromy terracotta army, carriages and horses were found in this pit (Liu, 2006). All the terracotta figures are one quarter or one sixth as large as the livings. They were arranged in a certain order to imitate the scene of a real situation. The figures of the terracotta army were made with different clothing style and painted in very well designed patterns. Fortunately, they are well preserved with bright colour; most of the colours used are red, white and purple. It is another great discovery after Qin Shihuang's terracotta army (259–210 BC), which definitely provides new evidence of the Han dynasty cloth style, the techniques of making pottery and colour paints etc. Archaeologists and art historians conclude the results of the new discovery and suggest that the Chinese in the Qin and Han dynasties probably made a regular practice of burying the bodies of their royals and nobles with a symbolic military escort. By comparing with the polychromy of Qin Shihuang's terracotta army, the size of Qingzhou Han dynasty terracotta army is smaller. Small terracotta armies were also found in other Han dynasty tombs, such as in Yangling, Shanxi and Xuzhou, Jiangsu province, which indicate the thought of the people in Han dynasty has changed in comparison to Qin dynasty. The people in Han dynasty started to use smaller terracotta figures as a symbol to achieve the same purpose as in Qin dynasty.

In the past, several studies of materials used for the polychromy of pottery in China have been reported. The earliest painted pottery found in Zhicheng county, Hubei province (4400–3300 BC), was studied resulting cinnabar as pigment on the pottery plate (Chen and Yang, 1984). Another important painted pottery was found in Dadiwang site (late Yang shao Culture, 3000 BC). The main pigments identified were chalk and cinnabar (Zheng, 1986), but until now little was known about the binding media in the paintings. Recently, egg was reported as binding medium used in polychromy Qin Shihuang's terracotta army (Bonaduce et al., 2008), while animal glue was identified as binding medium in Dunhuang wall paintings by HPLC technique (Li, 1995; Su, 2000), as well as in the wall paintings from Tang dynasty tombs (Wei et al., 2011a). In order to compare the techniques and materials used in paints in different periods and to provide scientific support for the protection of those valuable cultural relics, two of the Han dynasty

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polychromy terracotta army and a horse excavated in Xiangshan, Qingzhou county are investigated in this study, which are depicted in Fig. 1a–c.

In the literature, a number of instrumental techniques were applied for the identification of pigments, such as X-ray Fluorescence Analysis (XRF) (Neelmeijer et al., 2000), X-ray Microanalysis in a Scanning Electron Microscope (SEM/EDX) (Manzano et al., 2000) or X-ray Diffraction (XRD) (Mantler et al., 2000). The study of pigments in Chinese artefacts, such as Chinese purple and blue also known as Han blue ($BaCuSi_4O_{10}$) and Han purple ($BaCuSi_2O_6$) by Raman and SEM has been reported (Ma et al., 2006). Han purple and Han blue are synthetic barium copper silicate pigments that were developed in China at least 2000 years ago. It is known that those pigments were in use by the late Western Zhou dynasty (800 BCE) until the end of the Han dynasty (Liu et al., 2007). Those pigments were found in artifacts of beads, earrings, and octagonal sticks, as well as in paint layers of the terracotta army from the Qin dynasty (221–207 BCE) and on wall paintings of Han dynasty tombs (206 BCE–220 CE) (Heinz et al., 2010). Recently, Chinese purple was also identified in the paint layer of those Han dynasty terracotta army (Zhang et al., 2010). The identification of organic materials is still a challenge due to the complexity of the organic compounds, which are not stable, thus making it necessary to use and combine information from several steps of investigations. The main techniques used for the characterization of binding media in artworks include Fourier Transform Infrared Spectroscopy (FTIR) (Capitelli and Koussiaki, 2006), High Performance Liquid Chromatography (HPLC) (Peris-Vicente et al., 2005), Gas Chromatography Mass Spectrometry (GC/MS) (Andreotti et al., 2006 and Marinach et al., 2004) and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) (Piccirillo et al., 2005 and Capitelli et al., 2002). As known, GC analysis requires the transformation of the polar and non-volatile organic compounds into more volatile ones and these derivatives, typically following a preceding extraction and hydrolysis step, can be identified. Common derivatization reagents for this task are N-methyl-N-(terbutyldimethylsilyl) trifluoroacetamide (MTBSTFA), (m-trifluoromethylphenyl) trimethylammonium hydroxide (TFTMAH) (Pitthard et al., 2006), and trimethyl sulfoniumhydroxide (TMSH) which have been reported being effective for the analysis of fatty acids (Baumer et al., 2009; Dron et al., 2004; Wei et al., 2011a). Similarly, hydrolysed amino acids from proteinaceous binders of paintings can be effectively derivatized by the use of MTBSTFA in pyridine (Colombini et al., 1998) and ethyl chloroformate (ECF) (Mateo Castro et al., 1997; Wei et al., 2011a; Valianou et al., 2011). The identification of proteins is based on the relative concentration of the stable amino acids (Schilling and Khanjian, 1996; Pitthart et al., 2010; Wei et al., 2011a). Moreover, proteomics methods were also applied to identify the proteinaceous binding medium in artworks (Leo et al., 2012).

Analytical techniques including FTIR, XRF, Py-GC/MS and GC/MS were applied in this scientific investigation. However they must be natural organic materials, such as: drying oil, resin, gum or proteinaceous materials. In order to cover a wide range of materials, different analytical methods were applied.

2. Experimental

2.1. Samples

During this study, two types of samples are used, especially for binding media analysis: reference samples made of drying oils, resins and proteinaceous materials including egg, casein and animal glue were prepared in the Conservation Science Department, Kunsthistorisches Museum, Vienna, Austria (Pitthard et al., 2006). Five samples were extracted from the two of the figurines (Fig. 1a, b) and were analyzed for pigment and binding medium identification. Additionally, one adhesive sample from the polychromy horse (Fig. 1c) was obtained – in order to investigate the adhesive material used (see Table 1).

2.2. Natural and artificial UV ageing

The reference samples were prepared by casting them in thin films on glass slides. Naturally aged samples were stored for five years in the laboratory at room temperature. In order to imitate the real samples (such as samples from the Han dynasty terracotta), the reference materials were artificially aged. By exposing the samples in a SOL 2 sunlight simulation chamber (Dr. K. Hönle GmbH UV Technologies, Munich, Germany) equipped with a Xenon lamp,

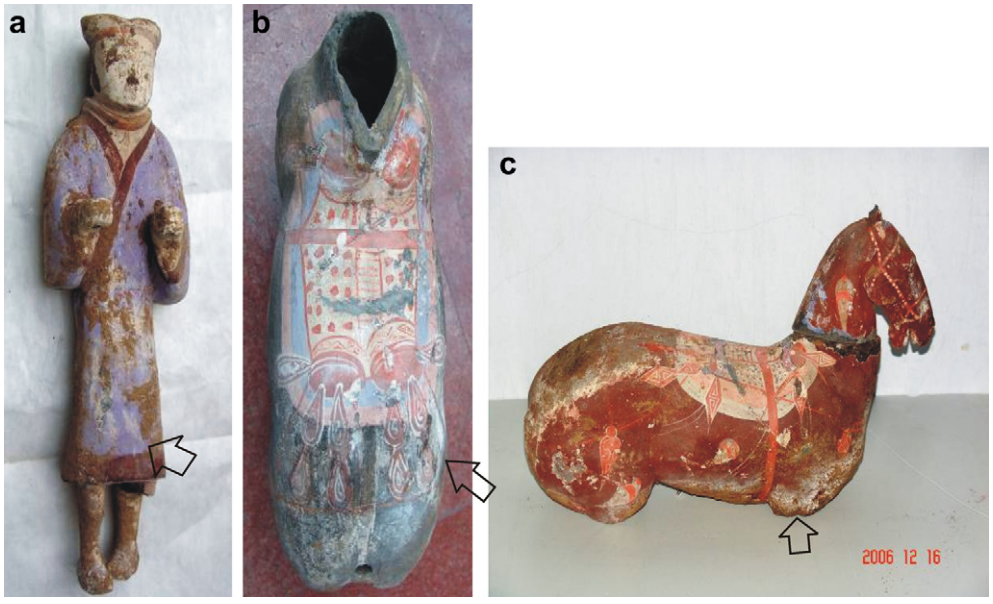

Fig. 1. a–c. Polychromy terracotta a) terracotta figure No. 286; b) terracotta figure No. 657; c) terracotta horse No.4. The arrows indicate where the samples were taken.

Table 1
Description of the six samples investigated.

Sample no.	Description of the samples	Archaeological no.
AH4	The adhesive to adhere the leg to the horse body No.4	$K_1(2)A_1$: No. 4 horse
P286	Purple paint from the skirt of standing terracotta No.286	$K_1X_2A_3$ 286
P657	Purple paint from the skirt of standing terracotta No.657	$K_1(2)A_6$ 657
W-P657	White preparing layer of No.P 657	$K_1(2)A_6$ 657
R657	Red paint from the skirt of standing terracotta No.657	$K_1(2)A_6$ 657
B657	Brown paint from the skirt of standing terracotta No.657	$K_1(2)A_6$ 657

offering light equivalent to the optical spectrum of sunlight with a luminescence of 120.000 lux and an irradiation intensity of 910 W m^{-2}. The reference materials were kept under these conditions for a period of 900 h (UV3).

2.3. Microscopy analysis

Microscopic studies should answer the question concerning the stratigraphy of the paint layer. Two small samples containing the whole layered structure of the terracotta were taken from the surface in order to prepare cross-sections. Therefore, specimen from the purple (MP1) and red (MR1) areas were embedded in epoxy resin, ground and polished after curing. The microscopic investigations were carried out using polarised light in the visible range in a microscope of Leitz, Germany, type Orthoplan.

2.4. X-ray fluorescence analysis

The X-ray fluorescence analysis was performed with an instrument Spectrace 5000 of Tracor, USA. The tube voltage and current were set at 30 kv and 0.02 mA, respectively. The measurements were carried out in air and the live time of 100 s for each spectrum was chosen.

2.5. FTIR analysis

The infrared spectroscopy investigations were performed with an instrument of Perkin Elmer, Germany Spectrum 2000, in combination with a microscope, i-series. For the analysis small grains of the samples were prepared and pressed in a diamond cell of Spctra-Tech, USA. The measurements could be done in the transmission mode and the evaluation and interpretation of the spectra was carried out by using the database of IRUG (Infrared and Raman Users Group, 2000).

2.6. Py-GC/MS

For the direct Py-GC/MS analysis, 0.1–0.2 mg of sample was placed in a sample cup. The cup was placed on top of the pyrolyzer at near ambient temperature and then introduced into the furnace by the auto sampler; afterwards the temperature program of the GC/MS was started.

The pyrolysis-gas chromatography/mass spectrometry measurements were carried out using a double-shot pyrolyzer PY-2010iD (Frontier Lab, Japan) attached to a gas chromatograph and mass spectrometry GC/MS-QP2010 Plus (Shimadzu, Japan). A capillary column SLB-5MS (5% diphenyl/95% dimethyl siloxane) with a 0.25 mm internal diameter, 0.25 μm film thickness and 30 m length (Supelco, USA) was chosen in order to provide an adequate separation of the components. The Shimadzu GC/MS is controlled by the real time analysis software package, where peak integration and mass spectra evaluation is included.

Pyrolysis was performed at 600 °C, the pyrolyzer interface was set at 320 °C and the injector at 250 °C. The chromatographic conditions were as follows: the oven initial temperature was 40 °C with a gradient of 10 °C min^{-1} to 300 °C, which was held for 20 min. The carrier gas was Helium with an inlet pressure of 15.5 kPa and 1:100 split ratio. The electronic pressure control was set to the constant flow mode. Ions were generated by electron ionisation (70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from m/z 50 to 750 with a cycle time of 0.5 s. EI mass spectra were acquired by total ion monitoring mode. The temperatures of the interface and the source were 280 and 200 °C, respectively. NIST 05 and NIST 05s Library of Mass Spectra were used for identifying the compounds.

2.7. GC/MS procedure

For GC/MS analysis, two steps of analysis were performed: in the first step, about 0.3 mg sample was taken, 50 μl of chloroform was added and shaken thoroughly; afterwards 25 μl trimethylsulfonium hydroxide (TMSH) reagent were added, ultra sonicated for 1 h and 2 μl of the solution were injected into the GC/MS for the identification of oils and/or resins. The residue from the first step analysis was evaporated to dryness. 60 μl of 6N HCl was added under argon to hydrolyze at 105 °C for 24 h. Afterwards, the hydrochloric acid was evaporated under a stream of argon at 70 °C. Then it was rinsed with distilled water and evaporated to dryness, repeated twice. 50 μl of pre-mixed solvent (water:ethanol:pyridine = 60:32:8) and 10 μl of ethyl chloroformate (ECF) reagent were added and shaken thoroughly; 50 μl of chloroform containing 1% ECF was added and shaken; 50 μl saturated $NaHCO_3$ solution was added and shaken. Finally, the mixture was centrifuged to obtain two clear separated phases. 2 μl of the organic phase were injected into the GC–MS for proteinaceous material identification. For the identification of

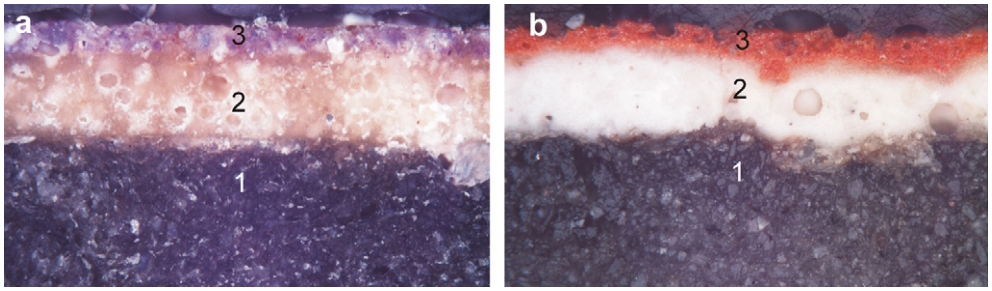

Fig. 2. Micrographs of the cross-sectioned of samples a) P286-purple paint with white preparation layer; b) R657-red paint with white preparation layer. 1- pottery layer, 2-white preparing layer, 3-purple/red paint layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

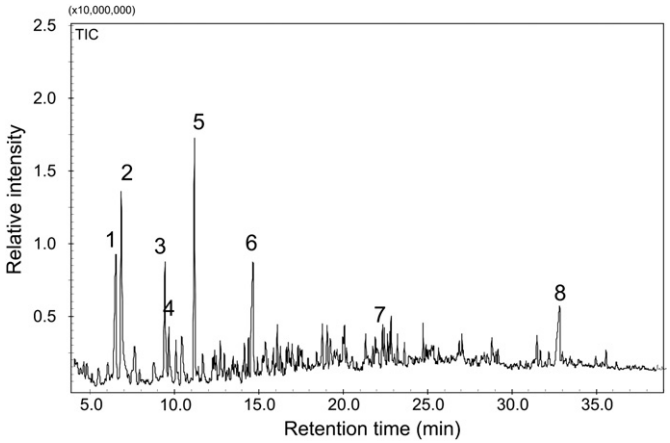

Fig. 3. TIC obtained by Py-GC/MS of sample AH4. 1: pyrrole; 2: toluene; 3: 2-methyl-1H-pyrrole; 4: 3-methyl-1H-pyrrole; 5: styrene, 6: 2-cyclohexen-1-one; 7: 5H-pyrrolo(3,2-d) pyrimidin-4-amine; 8: hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione.

proteinaceous materials GC–MS analysis, a capillary column SLB-5MS was employed. A temperature programme was used, initially keeping the column at 100 °C for one minute, followed by gradients of 5 °C per minute to 300 °C for nineteen minutes. The electronic pressure control was set to a constant flow of 1.0 ml/min in splitless mode. The injector temperature was set to 300 °C. MS parameters were chosen as for the Py-GC-MS analysis.

3. Results and discussion

3.1. Cross- sections of the paints and microscopy analysis

The images of the two cross-sections (samples of MP1 and MR1) with purple and red paints from the polychromy terracotta are shown in Fig. 2a and b, respectively. The pigment layers can be seen clearly on top and underneath the paint layer is a white fine preparation layer in both cases.

3.2. XRF analysis of the polychromy terracotta samples

XRF qualitative analyses were carried out directly on the surface of the paint samples and the white preparation particles (not on the cross-section samples). The results obtained by XRF are summarized in Table 2, the elements present as main constituents are in bold. In combination with the Raman analysis (Zhang et al., 2010), the pigments present can be concluded from the elemental composition. The relative concentration of mercury and lead is high in the red paint sample R657, indicating the presence of cinnabar and red lead, although the other main composition of cinnabar – sulphur is not detected due to the limit of the XRF instrument (which was operated in air not in vacuum condition). While in sample B657, the main elements detected are iron and calcium, only trace of mercury and lead were found, represent the main pigments are ochre and chalk. The pigments in samples of P286 and P657 are identified as Chinese purple and chalk. In addition, chalk was found as the material used in the white preparation layer (sample W-P657), which is the common material used for preparation layer for wall paintings in ancient times, such as the wall paintings in Tang dynasty (Wei et al., 2011a). Furthermore, the filling material in the adhesive (sample AH4), was also found as calcium carbonate.

3.3. FTIR

The FTIR analysis of sample AH4 reveals the following bands: the N–H stretching band at 3400–3200 cm^{-1}, C–H stretching bands at 3100–2800 cm^{-1}, C=O stretching band at 1660–1600 cm^{-1}, C–N–H bending band at 1565–1500 cm^{-1} and the C–H bending band at 1480–1300 cm^{-1}. These bands are typical for the presence of proteinaceous materials (Derrick et al., 1999). Unfortunately, the FTIR analysis of the other samples in Table 1 did not yield valuable spectra and no identification of the binding media present was probably due to the too low concentration of organic materials in the paint layers.

3.4. Py-GC/MS analysis

Py-GC/MS analysis on the reference materials of natural organic materials including drying oil, resin, lacquer and proteinaceious materials have been conducted in our lab (Pitthart et al., 2010; Wei et al., 2011b, c). To apply the knowledge to the two samples of AH4 and R657 (the amount of those samples allowed to carry out Py-GC/MS as well as GC/MS analysis). The total ion chromatogram of sample AH4 is depicted in Fig. 3. The main compounds identified are pyrrole (*m*/*z* 67), hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione (*m*/*z* 154), toluene and isoindole, 3-methyl-1H-pyrrol. They are the marker pyrolysis products of proteins by comparing to our reference proteinaceous materials, which are reported in the literature (Tsuge and Matsubara, 1985; Chiavari and Galletti, 1992). The detection of those compounds indicates the presence of proteinaceous material in the sample. However, in chromatogram of red paint sample RP 657 obtained by Py-GC/MS, the dominant peak is mercury (Hg), which was identified with the most abundant isotopes of the element: *m*/*z* 199, 200, 202 (Fig. 4). This result represents that cinnabar is most likely the red pigment in this sample, which is in agreement with the results obtained by XRF analysis. No characteristic organic materials were detected in this sample, probably due to the too low amount of the binding medium in the sample (as only 0.1 mg sample material is available for this analysis).

3.5. GC/MS analysis

The method described in Chapter 2.6 allows the analysis of both, the oil and protein-based fraction in binding media in one micro-sample, in a sequential way. It was applied for the unaged and artificially aged reference samples of oils, resins and proteinaceous

Table 2
XRF results and pigments identified (elements in bold are present as main constituents).

Sample no.	Colour	Elements detected by XRF	Substances identified	Pigments
AH4	Adhesive with white filling	**Ca**, Fe, Sr, K, Ti, Cr, Mn, Cu, Zn	$CaCO_3$	Chalk
P286	Purple paint	**Cu**, Pb, **Ba**, **Ca**, Fe, Sr	$BaCuSi_2O_6$, $CaCO_3$	Chinese purple, chalk
P657	Purple paint	**Cu**, Pb, **Ba**, **Ca**, Fe, Sr	$BaCuSi_2O_6$, $CaCO_3$	Chinese purple, chalk
W-P657	White preparation layer	**Ca**, Fe, Sr, K, Ti, Cr, Mn, Cu, Zn	CaCO3	Chalk
R657	Red paint	**Pb**, **Hg**, Fe, Ca, Cu	Pb_3O_4, HgS	Cinnabar, red lead
B657	Brown paint	**Fe**, **Ca**, Ba, Zr, Hg, Pb, Cu, K	Fe_2O_3, $CaCO_3$	Ochre, chalk

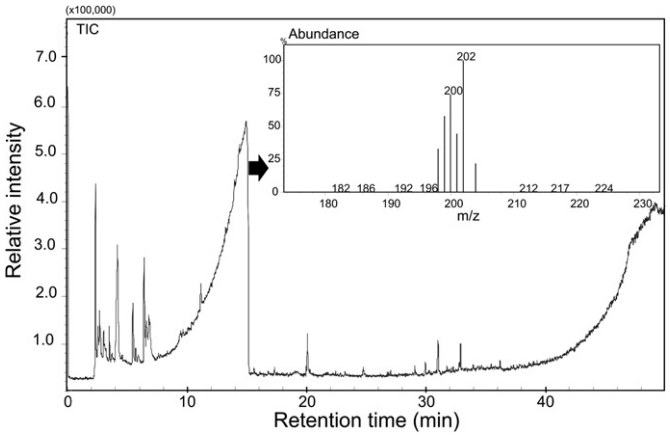

Fig. 4. TIC obtained by Py-GC/MS of sample R657 (red pigment) with the mass spectrum of mercury.

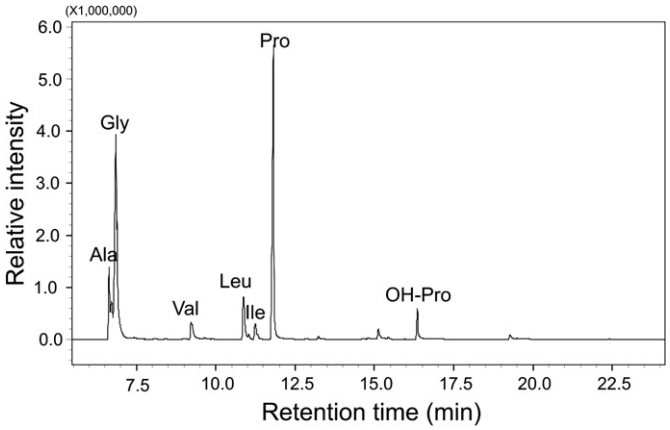

Fig. 5. Chromatogram of sample AH4 after hydrolysis and derivatized with ECF by GC/MS with SIM; OH-Pro: Hydroxyproline, Ala: alanine, Gly: glycine, Val: valine, Leu: leucine, Ile: isoleucine and Pro: proline.

materials. Drying oil can be characterized by their typical value of azelaic acid to palmitic acid (A/P) and palmitic to stearic acid (P/S), while resins can be identified by the detection of their marker compounds (such as in pine resin: dehydroabietic acid, 7-oxo-dehydroabietic acid and 15-hydroxy-7-oxo-dehydroabietic acid could be detected in the aged reference samples). The methods have been applied in case studies and the results were published recently (Valianou et al., 2011; Wei et al., 2011a). However, in the first step of this study, no characteristic information for drying oils or resins were found, which indicates that such materials are not present in the studied samples.

In order to characterize the proteinaceous material, the content of the GC vial used for the analysis of the lipid fraction was evaporated, hydrolysed with 6N HCl and subsequently derivatized with ethyl chloroformate (ECF) prior to GC/MS analysis. Amino acids have been identified in all six samples listed in Table 1 and their relative concentrations are summarized in Table 3. The analysis of (aged) proteinaceous binding media in painted works of arts is hampered by the fact that some of the naturally occurring amino acids are prone to metal-catalysed oxidation or decomposition. These include particularly the sulphur-containing amino acids cysteine, cystine and methionine, the heterocyclic amino acids histidine and tryptophan, and tyrosine. For this reason, classification of the binding media is typically based on the relative concentration of the stable amino acids including glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), proline (Pro) and sometimes also hydroxyproline (OH-Pro) (Schilling and Khanjian, 1996; Gimeno-Adelantado et al., 2002). Although relative ratios may change with time, and also may be interfered in the presence of certain inorganic pigments, some ratios are very characteristic and were used to assign the type of binding medium.

The assignment of the proteinaceous medium in the six samples is based on the relative concentrations of the stable amino acids. According to the experiments results, the concentration of the unstable amino acids and the unsaturated fatty acids in egg are significantly decreased in the aged sample in comparison with the unaged ones. Especially, the concentration of marker compound of animal glue-hydroxyproline significantly decreased after ageing. According to the experiment results, the data of aged reference materials are more comparable with the archaeological samples, which are present in Table 3. These allow in the present case the assignment of the proteinaceous binding media (Table 3). The high fraction of glycine (Gly) with respect to alanine (Ala), as well as the high levels of proline (Pro) and low levels of valine (Val) prompt us to suggest the presence of animal glue in all investigated samples.

Hydroxyproline is the marker compound for the protein of animal glue (Schilling and Khanjian, 1996 and Colombini et al., 1998), but it is not found in the TIC of the samples obtained by GC/MS analysis. In order to improve the sensitivity of the analysis, select ion mode chromatography (SIM) was also carried out. The selected ions including alanine (m/z 116), glycine (m/z 102), valine (m/z 144), leucine (m/z 158), isoleucine (m/z 158), proline (m/z 142) and hydroxyproline (m/z 158) were chosen. The SIM chromatogram of sample AH4 obtained by GC/MS after hydrolysis and derivatized with ECF is depicted in Fig. 5. Apart from the amino acids found in TIC, hydroxyproline (OH-Pro) was also detected in the sample with SIM, which gives additional support of the conclusion that animal glue is the adhesive material. It has to be mentioned that hydroxyproline could not be detected in other samples with SIM, probably due to the low concentration or highly degraded situation. In summary, according to the relative concentration of the stable amino acids, the presence of animal glue is suggested for the six samples.

Table 3
Relative concentration of stable amino acids in the six samples (normalized). The values of reference samples for animal glue, egg yolk and casein were obtained in samples after artificial ageing.

Samples from the terracotta							Reference samples		
Amino acids %	AH4	PP286	PP657	W-PP657	RP657	BP657	Animal glue	Egg yolk	Casein
Ala	15.8	16.8	20.8	13.2	23.4	16.1	16.9	19.7	8.6
Gly	33.6	32.8	29.8	35.6	25.2	45.7	43.9	14	7.6
Val	5.5	7.1	7.1	4.2	6.1	0.8	5.0	20.3	8.6
Leu	6.1	9	9	6.1	4.6	4.1	6.8	25.8	20.8
Ile	4.4	3.9	3.9	4.9	4.2	3	2.5	13.8	5.3
Pro	34.5	30.5	29.5	36	36.4	30.3	25.0	6.3	49.1
Assignment	animal glue	animal glue	animal glue	animal glue	animal glue	animal glue			

4. Conclusion

The materials used for the Han dynasty polychromy terracotta army have been analyzed by optical microscopy, XRF, Py-GC/MS and GC/MS. The results reveal that the paint layer was applied after a white preparation layer on the surface of the terracotta substrate. The materials used for the white preparation layer is chalk. Pigments used are Chinese purple, cinnabar, red lead and ochre. Animal glue was found in all the six samples indicating that it was used as binding medium for both of white preparation layer and in the paint layer. It also was applied as adhesive material to adhere the leg to the polychromy horse body with filling materials of chalk. In comparison with Qin Shihuang's terracotta army, the pigments including the Chinese purple, cinnabar were found in both of Qin and Han dynasty terracotta, but the binding media used are different. In Qin Shihuang's terracotta army egg was reported as binding medium (Bonaduce et al., 2008). However, in our study animal glue was identified as binding media as well as adhesive, which is in agreement with the historical book of "Zhou Li Dong Guan Kao Gong Ji" (Warring States period 475–221 BC). In this book, animal glue including deer glue, ox skin glue and horse glue are described as binding media. It will be very interesting for further study about what are the binding media used for paintings in different dynasties.

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