

## THE IDENTIFICATION OF THE BINDING MEDIA IN THE TANG DYNASTY CHINESE WALL PAINTINGS BY USING Py-GC/MS AND GC/MS TECHNIQUES

Shuya WEI<sup>1\*</sup>, Manfred SCHREINER<sup>1</sup>, Erwin ROSENBERG<sup>2</sup>, Hong GUO<sup>3</sup>, Qinglin MA<sup>3</sup>

<sup>1</sup>) Institute of Natural Sciences and Technology in Art, Academy of Fine Arts, Vienna, Austria

<sup>2</sup>) Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Austria

<sup>3</sup>) Chinese Academy of Cultural Heritage, Chao Yang District, Beijing, China

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### Abstract

*The archaeological discoveries of Tang tomb murals in Xi'an, China brought to light unprecedented data for the study of the art of the Tang Dynasty (618-907 AD). The spectacular murals with their particular contents provided first-hand material for the study of Chinese history and the techniques of wall paintings during the Tang Dynasty. In order to gain a better understanding of the materials used and to preserve those paintings, pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) and gas chromatography-mass spectrometry (GC/MS) were applied for the characterization of the binding media in the paintings. The combination of these analytical techniques is an ideal methodology to identify binding media in unknown samples.*

**Keywords:** wall painting; binding media; plant gum; linseed oil; pine resin; animal glue.

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### Introduction

The archaeological discovery of the Tang tomb murals in Xi'an, China have brought to light unprecedented data for the study of the art during the Tang Dynasty (618-907 AD). They are an inexhaustible encyclopedia which provides first-hand material for the study of the history, social life and painting techniques in the Tang Dynasty. After their excavation, the murals were detached from the tomb chambers and stored in Shanxi History Museum. The paintings amounted to about 1000 m<sup>2</sup> of painted area and they were collected from nearly twenty Tang tombs, by removing the layer of the upper 0.5-1 cm of the murals off the tomb walls. The systematic analytical investigation described in this report has been carried out in the frame of the cooperation project 'Rescue and Conserve the Endangered Wall Paintings in the Museums of China'. The knowledge of the original materials used in the painting, as well as the conservation intervention is essential for ensuring appropriate conservation and maintenance procedures. In regard to the conservation of Chinese wall paintings, different consolidation materials were used during the past decades, such as peach gum, polyvinyl acetate (PVAc) and polyvinyl butyral (PVB) [1]. However, there is no documentation available about the conservation treatments on the investigated wall paintings. Since the aim of this study is to characterize materials from works of art, the analytical method must be as minimally invasive as possible.

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\* Corresponding author: sywei66@hotmail.com, +43-1-58816-8615

Similar studies mention gas chromatography-mass spectrometry (GC/MS) [2, 3] and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) [4, 5] as well established techniques for the characterization of binding media, as well as for varnishes in artworks. In recent studies about Chinese relics, animal glue was identified as a binding medium in the Dunhuang mural paintings [6, 7], while egg was found as binder in the polychrome terracotta army of Qinshihuang [8]. However, most of the methods focused on the identification of one or two specific substances. In this study, the analysis methodology had to cover the restoration materials as well as the original materials used in the wall paintings. The original binding media could be only natural organic materials such as drying oils, proteinaceous materials, natural resins etc. due to the unavailability of synthetic techniques in ancient time. The conservation intervention materials could be synthetic resins or natural organic materials. Py-GC/MS, which is an ideal technique for the identification of synthetic organic materials was used to identify possible conservation intervention materials, [9, 10] (although we did not find synthetic materials in the samples); GC/MS following a two-step derivatization procedure were applied for the identification of natural organic materials in the wall paintings.

**The two-step derivatization procedure for GC/MS analysis:** In the first step, samples are derivatized with trimethylsulfonium hydroxide (TMSH) reagent for the identification of oils, resins [11, 12]. The procedure enables the quantitative analysis of fatty acids, which subsequently makes the classification of various types of oil possible, based on A/P (aezlaic acid to palmitic acid) and P/S (palmitic acid to stearic acid) ratios. Although terpenic resin compounds contain hydroxyl groups, that cannot be derivatized with TMSH reagent, the procedure enables the identification of the marker compounds of resins. In the second step of the analytical procedure, the sample residue from the first step analysis is evaporated to dryness, hydrolyzed and then derivatized with ethyl chloroformate (ECF) reagent for the quantitative analysis of amino acids [13, 14]. Based on the relative composition of amino acids, classification of different proteinaceous materials can be achieved. The procedure was adopted from Gimeno-Adelantado et al. [15] and slightly modified. It was validated on reference data and applied on the identification of the binding media used in artworks [16, 17].

The two-step analytical procedure is relatively simple with a minimum of sample handling and transfer steps, thereby avoiding loss, or contamination of the precious sample. The developed procedure intends to identify the different materials potentially present within a single, small sized sample, on the basis of characteristic tracer compounds. Therefore, it is not necessary to comprehensively detect all compounds present in a given sample. The two techniques Py-GC/MS and GC/MS complement each other to cover a wide range of materials potentially present in samples. They were successfully applied for the identification of different organic materials in the wall paintings.

### *Description of the wall painting samples*

Nine paint samples with ground layer (about 2 mg each) were taken with a scalpel from the wall paintings of Weishi's tomb (?-656 AD), the tomb of the crown Prince Zhanghuai (654-684 AD) and from Lishuang (593-668 AD) tomb for analysis. Figures 1 a-c depict the three images of the wall paintings from the three tombs which were investigated and also introduce the labeling of the samples as B185-1, B185-2; B113-1 to B113-5; B31-1 to B31-3, according to the mural from which the samples were taken. A short description of the samples is given in table 1.



**Fig.1.** Photographs of: a - The wall painting of Weishi's tomb (B185);  
b - The wall painting from prince Zhanghuai's tomb (B113) and  
c - The wall painting from Li Shuang's tomb (B31).

**Table 1.** Descriptions of the samples analyzed

No.	Colour	Location
B 185 -1	Green powder	From the green area of a servant lady in Weishi's tomb.
B 185 -2	Red with ground	Collected in Weishi' tomb
B 113 -1	Red paint	From the right corner, in Zhanghuai's tomb
B 113 -2	White paint	Right upper corner, in Zhanghuai's tomb
B 113 -3	White paint	Right lower corner, in Zhanghuai's tomb
B 113 -4	Black with ground	From one boot of a man, in Zhanghuai's tomb
B 113 -5	Dark red paint	From the skirt of a lady, in Zhanghuai's tomb
B 31 -1	Red paint	Left corner of a servant lady with a plate in hands, in Li Shuang's tomb
B 31 -2	Black paint	From the foot of a servant lady with a plate in hands, in Li Shuang's tomb

## Experimental

### *Reference materials*

A series of mock-ups were prepared in the Conservation Science Department, Kunsthistorisches Museum, Vienna, by mixing the binding media with different pigments, spreading the mixtures on glass slides and allowing them to dry in daylight at room temperature as unaged samples. Parts of the mock-ups were subjected to artificial ageing. Details about the mock-ups are reported in [18]. The following natural materials, synthetic resins and emulsions supplied by Kremer (Aichstetten/ Allgäu, Germany) were used as reference materials:

- 1) Drying oils: linseed oil, linseed stand oil, poppy seed oil, walnut oil;
- 2) Proteinaceous materials: animal glue, casein, fish glue, egg;
- 3) Natural resins: sandarac, Manila copal, Strasbourg turpentine, amber, dammar, mastic;
- 5) Gums: peach gum, cherry gum, Tragacanth, Arabic gum;
- 6) Synthetic materials: Primal 35 [(p EA/MMA)], Plextol D 498[(p (n BA/MMA))], Rohagit SD15 [ p(EA/EMA)].

### ***Sample preparation for binding media identification***

Since Py-GC/MS did not require any particular sample preparation, for this type of analysis small amounts of samples (about 0.2 mg) were set into the sample cups and the specimens were introduced by the auto sampler directly into the Frontier Lab pyrolyzer. The volatile pyrolysis products were analyzed by GC/MS.

For GC/MS analysis, the following two step analytical procedure was performed: in the first step, about 1.0 mg sample was taken, 50  $\mu$ l of chloroform was added and the mixture shaken thoroughly, afterwards 25  $\mu$ l trimethylsulfonium hydroxide (TMSH) reagent (0.25 M in MeOH; obtained by Macherey-Nagel, Düren, Germany) was added, ultrasonicated for 1 hour and 2  $\mu$ l of the supernatant solution were injected into the GC/MS for the identification of oils, resins and waxes. In a second step, the sample residue from the first step (both MeOH extract and the solid residue) was evaporated to dryness. 60  $\mu$ l of 6N HCl were added and the sample allowed to hydrolyze at 105 °C for 24 hours under argon. Afterwards, the hydrochloric acid was evaporated under a stream of argon at 70 °C. Then the residue was rinsed with distilled water and evaporated to dryness, which was repeated twice. 50  $\mu$ l of pre-mixed solvent (water : ethanol : pyridine = 60 : 32 : 8) and 10  $\mu$ l of ethyl chloroformate (ECF) reagent (obtained from Fluka, Buchs, CH) added and shaken thoroughly; 50  $\mu$ l of chloroform containing 1% ECF were added and shaken; 50  $\mu$ l saturated NaHCO<sub>3</sub> solution was added and shaken. Finally, the mixture was centrifuged to obtain two clear, separated phases. 2  $\mu$ l of the organic phase was injected into the GC/MS for proteinaceous material identification. It is worth noticing here that, although fatty acids can also be detected in the second step, they were not used for calculating the A/P and P/S ratios, due to the random distribution of the derivatives between the two phases (organic and aqueous) makes quantitative analysis impractical. The fatty acids are quantitatively determined from the first step which gives more reliable results.

### ***Instruments and parameters***

For the analyses of the samples, a double shot pyrolyzer type PY-2010iD of Frontier Lab, (Fukushima, Japan), and a gas chromatograph-mass spectrometer, GC/MS-QP 2010 Plus of Shimadzu (Kyoto, Japan) were employed. Shimadzu GC/MS real time analysis software was used for GC-MS control, peak integration and mass spectra evaluation. The pyrolysis was performed at 600 °C for 10 s. The pyrolyser interface was set to 320 °C and the injector to 250 °C, respectively. A capillary column SLB-5MS (5% diphenyl / 95% dimethyl siloxane) of 0.25 mm internal diameter, 0.25  $\mu$ m film thickness and 30 m length (Supelco, PA, USA) was used in order to provide adequate separation of the components. The chromatographic conditions were as follows: The oven initial temperature was set to 40 °C for five minutes, then followed by a gradient of 6 °C per minute up to 292 °C (hold for three minutes; total run time: 50 min). The carrier gas used was Helium (He, purity 99.999%). The electronic pressure control was set to a constant flow of 0.6 ml/min, in split mode at 1:40 ratio. The mass spectrometer operated in the EI positive mode (70 eV) and MS spectra were recorded in TIC (total ion current), scanned in the range from m/z 50 to 750, with a cycle time of 0.5 seconds. The temperatures of the interface and the source were 280 °C and 200 °C, respectively. NIST 05 and NIST 05s Libraries of Mass Spectra were available for the identification of the compounds. Since no information were available on the materials used in previous conservation treatment of those wall paintings, which could either be synthetic polymers or natural organic substances, the pyrolysis program was adopted from the identification of synthetic materials [9], slightly changed and validated for both synthetic and natural material analysis [19, 20].

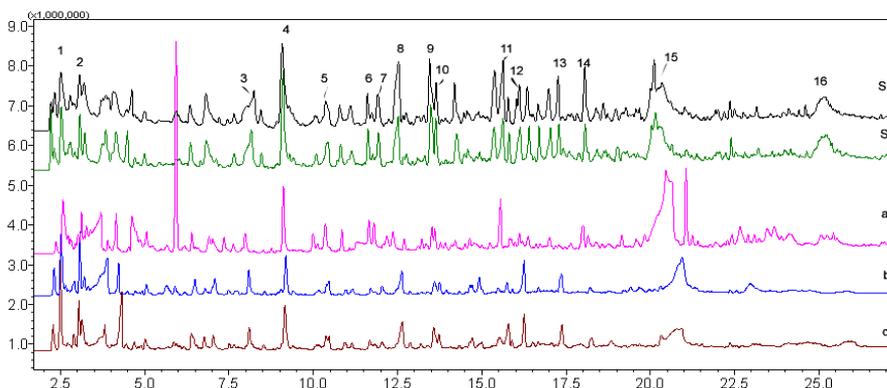
For the GC/MS analysis of the derivatives obtained in the first step of the sequence, a capillary column SLB-5MS was employed. The chromatographic conditions were as follows: The oven initial temperature was set to 50 °C, then followed by a gradient of 8 °C per minute up to 298 °C, held for nineteen minutes (total run time: 50 min). The carrier gas used was Helium. The electronic pressure control was set to a constant flow of 0.8 ml/min, in splitless mode. The injector temperature was set to 250 °C. The MS parameters were the same as for the Py-GC/MS analysis.

The GC/MS analysis of the derivatives resulting from the second step of the sequence was performed with the same SLB-5MS capillary column, but with a different temperature programme: initially keeping the column at 100 °C for one minute, followed by a gradient of 5 °C per minute to 300 °C for nineteen minutes (total run time: 44 min). 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.

## Results and discussion

### *Analysis results obtained by Py-GC/MS*

The evaluation of the results obtained by Py-GC/MS of the wall painting samples was done by comparing these with the reference data base of our laboratory, which includes a wide range of synthetic conservation materials and natural organic materials (e.g. peach gum, Tragacanth and Arabic gum). The pyrolysis chromatograms of peach gum, Tragacanth and Arabic gum, as well as from sample B113-2 are depicted in figure 2. In order to see the reproducibility of the analysis, two chromatograms obtained by Py-GC/MS on different portions of the same sample B113-2 are shown in figure 2 (S1 and S2).



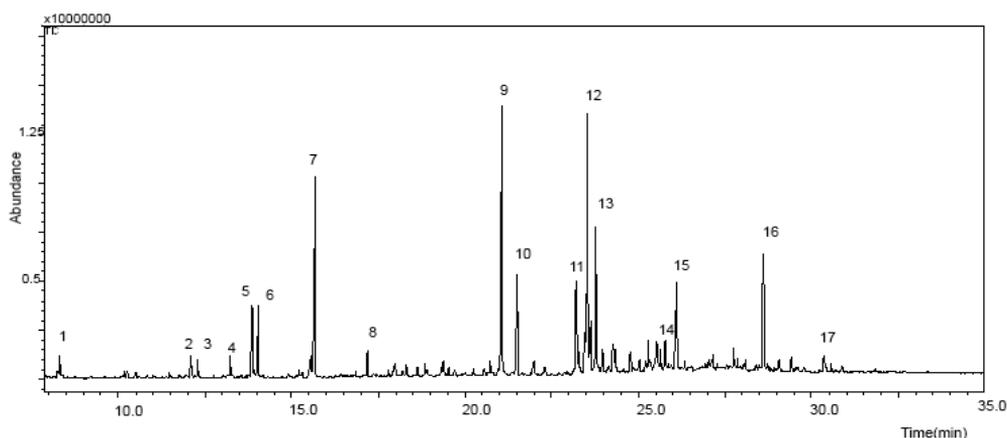
**Fig. 2.** TIC chromatogram obtained by Py-GC/MS of S1 - Sample B113-2 first analysis; S2 - Sample B113-2 second analysis; a - peach gum; b - Tragacanth gum; c - Arabic gum.

It becomes evident that the analysis has good reproducibility. Comparing the Py-GC/MS chromatograms of the sample and the reference materials, the main peaks found in the sample are also present in the gums that have been investigated as reference substances. It can thus be concluded that plant gum is present in the sample. This finding is in agreement with previous studies [21], since peach gum was normally used as a consolidation material to strengthen the wall paintings during their detachment from the wall. Plant gums are complex polysaccharides obtained from a variety of different vegetables. The polysaccharides contained in the gums

comprise various units of sugars (aldohexoses and aldopentoses) and uronic acids. According to the peak pattern and intensities in different types of natural gums by pyrolysis analysis, the gums could be classified [19, 22]. However, when we confronted with mixture of gum and other organic materials, it is difficult to identify a specific gum by direct Py-GC/MS analysis. If more precise classification of the gums is needed, chemical hydrolysis followed by GC or LC analysis could be used [23, 24]; while pyrolysis with on-line derivatization with tetramethylammonium hydroxide (TMAH) [25, 26] and silylation with hexamethyldisilazane (HMDS) could also be applied [27, 28]. That is out of the range of this study.

### *The identification of oil and resins by GC/MS*

The identification of oils and resins by GC/MS analysis is based on detection of their trimethylsulfonium hydroxide (TMSH) derivatization products, which are the respective methyl esters [11]. The drying oil can be identified through the detection of the oxidation products from the unsaturated fatty acids of the oil as well as the ratio of the oxidation product azelaic acid to palmitic acid (A/P) and palmitic acid to stearic acid (P/S) [29, 30]. Resins [31] and waxes [32] can be identified according to their marker compounds and special constituents. After derivatization with TMSH, the samples were subjected to GC/MS analysis. Drying oil was identified in samples B185-2, B31-1 and B31-2. As an example, the chromatogram of sample B31-1 is depicted in figure 3 and the compounds identified are listed in table 2. Compounds detected including octanoic acid, 8-oxo-octanoic acid, heptanedioic acid, 8-hydroxy-octanoic acid, 9-oxo-nonanoic acid, suberic acid, azelaic acid (A) and sebacic acid are known as oxidation products from unsaturated fatty acids in drying oils. Palmitic (P) and stearic acids (S) are saturated fatty acids, which are stable during the ageing process. The values of A/P and P/S peak area ratio are 0.8 and 1.2, respectively for the samples B185-2, B31-1 and B31-2. The comparison of these values with the ratios obtained for reference materials suggest the presence of linseed oil [11]. Since phthalates are widely used as plasticizers in any type of plastic materials, the observed signal in the chromatogram could result from contamination. In addition, dehydroabietic acid ( $m/z$ : 239, 299), 7-oxo-dehydroabietic acid ( $m/z$ : 253, 328) and 15-hydroxy-7-oxo-dehydroabietic acid ( $m/z$ : 269, 329) were also detected in the three samples, which are the marker compounds of aged diterpenoid resin [17, 33]. The detection of these compounds points to the existence of pine resin.



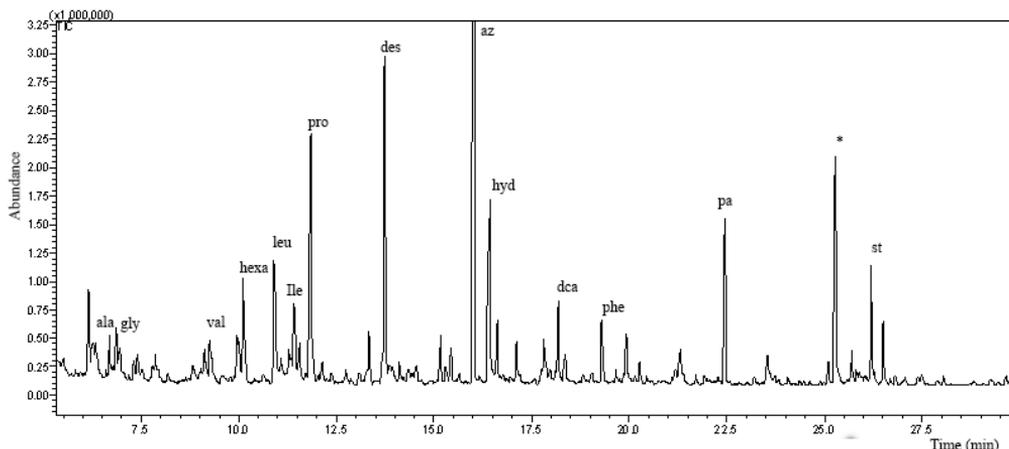
**Fig.3.** TIC chromatogram obtained by GC/MS of sample B31-1 after derivatization with TMSH; compounds identified (peak no. 1-17) are listed in table 2.

**Table 2.** Compounds identified in sample B31-1 by GC/MS analysis after derivatization with TMSH

Peak No.	RT [min]	Area %	Compounds identified
1	8.31	1.9	Octanoic acid methyl ester
2	12.10	1.2	8-oxo-octanoic acid methyl ester
3	12.29	0.9	Heptanedioic acid dimethyl ester
4	13.24	1.1	8-Hydroxy-octanoic acid, methyl ester
5	13.86	4.3	9-oxo-nonanoic acid, methyl ester
6	14.03	4.8	Suberic acid, dimethyl ester
7	15.67	13.8	Azelaic acid, dimethyl ester
8	17.18	1.4	Sebacic acid, dimethyl ester
9	21.06	17.9	Palmitic acid, methyl ester
10	21.50	5.9	Dibutyl phthalate
11	23.22	4.9	Oleic acid, methyl ester
12	23.54	15.4	Stearic acid, methyl ester
13	23.78	9.7	Unidentified
14	25.78	1.8	Eicosanoic acid, methyl ester
15	26.11	8.7	Dehydroabietic acid methyl ester
16	28.61	7.6	7-oxo-dehydroabietic acid, methyl ester
17	30.36	1.0	15-Hydroxy-7-oxo-dehydroabietic acid, methyl ester

### *The identification of proteinaceous materials by GC/MS*

The proposed procedure was used to analyze the reference materials: animal glue, casein and whole egg. In order to see the influence of the pigments to the identification of the proteinaceous materials, mock-up samples of whole egg mixed with different pigments (lead white, titanium white, azurite, burnt umber ) before and after accelerated UV aging were analyzed. The results were that the identification of proteinaceous materials based on the proportion of stable amino acids (alanine, glycine, valine, leucine, isoleucine and proline) are unaffected by pigments or aging, which is in agreement with studies published by other authors [15, 34, 35]. Following the procedure described in sample preparation section the second step GC/MS analysis for the identification of proteinaceous materials, the Amino acids were detected in two of the samples (B31-1 and B113-1). As an example the total ion chromatogram obtained by GC/MS analysis of sample B31-1 after hydrolysis and derivatization with ECF is shown in figure 4. The compounds identified and their relative concentration are listed in table 3. Apart from the amino acids as their N-carboxyethyl-amino acid ethyl esters, fatty acids including suberic acid (des), azelaic acid (az) and sebacic acid (dca), palmitic acid (pa) and stearic (st) acids were also detected in this step as their ethyl esters. They are the oxidation products and original compounds from drying oil. However they were not used for the classification of oils due to their distribution between the two phases, which does not make their quantitative analysis feasible (The classification of drying oils have been achieved in the first step GC/MS analysis).



**Fig.4.** TIC chromatogram obtained by GC/MS of sample B31-1 after hydrolysis and derivatization with ECF; compounds identified are listed in table 3.

**Table 3.** Compounds identified in sample B31-1 by GC/MS analysis after hydrolysis and derivatization with ECF; Note: EE- the derivatives of the amino acids or fatty acids with ethyl chloroformate, that are the N-carboxyethyl-amino acid ethyl esters and fatty acid mono- and diethylesters respectively

Peak	RT [min]	Area %	Identified compounds
ala	6.68	1.1	Alanine EE
gly	6.85	1.0	Glycine EE
val	9.26	1.2	Valine EE
hexa	10.11	4.8	Hexanoic acid, anhydride
leu	10.91	5.6	Leucine, EE
Ile	11.28	0.5	Isoleucine EE
pro	11.84	11.7	Proline EE
des	13.74	10.3	Suberic acid EE
az	16.02	32.1	Azelaic acid EE
hyd	16.42	9.3	Hydroxyproline EE
dca	18.17	2.3	Sebacic acid EE
phe	19.30	2.2	Phenylalanine EE
pa	22.44	5.8	Palmitic acid EE
st	26.197	3.8	Stearic acid EE
*	25.271	8.5	(m/z 177, 250, 296) unidentified

The average stable amino acid values (percentage) for three independent replicas of reference materials as well as the two samples (B31-1 and B113-1) by GC/MS analysis are listed in table 4. The table shows that egg has highest concentration of leucine, casein has highest concentration of proline, while animal glue contains an abundance of glycine, proline and hydroxyl proline. In particular, hydroxyproline is only present in animal glue. Those findings are in compliance with previous relevant studies [13-15, 33-36]. By comparison with the reference materials, it can be concluded that animal glue is present in the two samples (B31-1 and B113-1).

**Table 4.** The stable amino acids and hydroxyproline percentage (normalized, average of three times analysis) in reference materials of egg, casein, animal glue, sample B31-1 and B113-1 by GC/MS analysis after hydrolysis and derivatized with ECF

Amino acid%	egg	casein	animal glue	B31-1	B113-1
Ala	18.2	7.6	9.8	3.6	11.6
Gly	13.6	7.0	40.4	3.3	31.0
Val	14.2	11.2	2.2	4.0	5.3
Leu	27.1	20.2	3.9	18.4	6.0
Ile	9.2	7.5	1.2	1.6	3.7
Pro	17.6	46.5	26.3	38.5	31.9
Hyd	-	-	16.3	30.5	8.5

## Discussion and Conclusions

Nine samples from the Tang Dynasty wall paintings were investigated by Py-GC/MS and GC/MS techniques. The consolidation materials used for previous conservation of the murals are confirmed as plant gum. Animal glue was found in two paintings from two tombs (in samples B31-1, B113-1), indicating that it could be the original binder of the paintings, according to historical literature [26]. It is the first time that linseed oil and pine resin were found in Tang Dynasty wall paintings (in samples B185-2, B31-1, B31-2). They could either be the original binding media or components of later conservation intervention. Further investigation is required.

The detection of these substances is extremely interesting in terms of the historical significance of the work of art itself as well as for conservation. The binding media used in samples of B113 -2, B113-3, B113-4, B113-5, B185-2 could not be identified due to the small amount of sample and the increased state of degradation. The combination of the Py-GC/MS technique and GC/MS following a simple, two-step derivatization procedure could cover a wide range of substances, so as to obtain comprehensive information about the binding media used in artworks with a minimum sample quantity.

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