INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 1, Issue 2, April-June 2010: 99-112 www.ijcs.uaic.ro

SCIENTIFIC INVESTIGATION OF THE MATERIALS IN A CHINESE MING DYNASTY WALL PAINTING

Shuya WEI[1*], Manfred SCHREINER[1], Hong GUO[2] , Qinglin MA[2]

[1)] Institute of Natural Sciences and Technology in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria
[2)] Chinese Academy of Cultural Heritage, No. 2 Gaoyuan Street, Chao Yang District, Beijing, 100029, China

Abstract:

In the frame of the cooperation project Rescue and Conserve the Endangered Wall Paintings in the Museums of China, systematic investigations concerning the materials and techniques used in the wall paintings detached from a Ming Dynasty (1368-1644) temple, Dazhao Temple in Hohhot, Inner Mongolia of China, as well as the previous conservation intervention materials have been carried out. X-ray Fluorescence Analysis (XRF), X-ray Diffraction (XRD), Scanning Electron Microscopy in combination with Energy Dispersive X-ray microanalysis (SEM/EDX) were used for the identification of inorganic materials in the wall paintings, while Pyrolysis in combination of Gas Chromatography Mass Spectrometry (Py-GC-MS) was applied for the characterization of organic materials. Pigments including cinnabar, lead white, atacamite/para-atacamite, orpiment, ochre, minium, carbon black and smalt were identified. The binding medium in the painting was determined as animal glue. Alkyd is an uncommon consolidant in the conservation of Chinese wall paintings, but it could be determined in this object, where conservation treatments were performed in the 1950s.

Keywords*: XRF; XRD; SEM/EDX; Py-GC-MS; Chinese wall painting; Dazhao Temple*

Introduction

The Dazhao Temple is the oldest building and the largest Lamaist Buddhist temple in Hohhot, Inner Mongolia of China. The construction of the temple was completed in 1580 during the Ming Dynasty (1368-1644). Although there was a major reconstruction in 1640, much of the original architectural style could be retained. It owns its fame to a visit by the third Tibetan Dalai Lama in 1586, when he dedicated it the Silver Buddha statue. As a consequence Hohhot became a religious center for people from all over Mongolia who came to worship at the temple. The "Three Marvelous Treasures" of the temple (The Silver Buddha, The Dragon sculpture and the wall paintings) are relics from the Ming Dynasty with religious, artistic and scientific values. The mural paintings are on the theme of Buddhism figures and stories, presenting all sorts of visions of heaven, the world and hell.

In the 1950s, the mural painting in one of the buildings was detached from the wall due to reconstruction activities. It was cut into twenty four irregular rectangular pieces. The total surface is approximately 4 m^2 (Fig. 1a). After detachment, the painting fragments were fixed to a piece of synthetic fabric, mounted on a wooden frame and stored in the Hohhot Museum. After several decades in the storage of the museum, problems such as cracks and paint flaking

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

occurred, due to the deformation of the wooden frame. The consolidation material on the back side of the painting migrated to the surface in some areas, especially at the cutting edges, which spoiled the whole presentation (Fig. 1b). Although the conservation and preservation of cultural heritage items started in China in the 1950s with high scientific support, there is no documentation available about any conservation intervention materials used in that case. In the frame of the project Rescue and Conserve the Endangered Wall Paintings in the Museums of China, research work was carried out focusing on a better understanding of the materials and techniques used for the paintings, as well as on any previous conservation interventions.

a b

Fig. 1. a) Wall painting of Dazhao Temple for the investigation,
b) Details of the conservation treatment material on the surface of the painting

The detached wall painting has a ground layer - a layer of plaster, a white preparation layer and paint layer. For the identification of the inorganic components in wall paintings a number of instrumental techniques such as X-ray Fluorescence Analysis (XRF) [1, 2], Proton Induced X-ray or γ-ray Emission Spectroscopy (PIXE, PIGE) [3], X-ray Microanalysis in a Scanning Electron Microscope (SEM/EDX) [4, 5], X-ray Diffraction (XRD) [6] or Raman Spectroscopy [7] are recommended by specialists. Nevertheless, the determination of the organic materials is still a challenge, due to the complexity of such compounds and their chemical stability. In theory, the main techniques used for the identification of binding media in artworks include Fourier Transform Infrared Spectroscopy (FTIR) [8, 9], High Performance Liquid Chromatography (HPLC) [10, 11], Gas Chromatography Mass Spectrometry (GC-MS) [12-16] and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) [17-20]. Methylation reagent tetramethylammonium hydroxide (TMAH) [21] and sililation reagent hexamethyldisilazane (HMDS) have been combined with Py-GC-MS analysis in recent studies [22].

For Chinese wall paintings, there are also more studies about pigments published, [23, 24] than analyses of the binding media. Concerning the conservation of Chinese wall paintings, several papers mentioned that different consolidation materials and techniques were used during the past decades [25, 26], such as peach gum, polyvinyl acetate (PVAc) and polyvinyl butyral (PVB) [27]. From the 1970s epoxy was the main consolidant applied to wall paintings [28], although its reversibility is poor. Recently, materials including polyvinyl alcohol (PVAL), polyamide [29] and gelatine were reported to be used as well [30, 31].

In this study, Polarized Light Microscopy (PLM), XRF, SEM/EDX, XRD and Raman Spectroscopy were applied for the examination of the painting technique and for pigment identification. At first, XRF analysis was performed for the identification of pigments, because it is non-invasive (no sampling). However, it can not be used to analyze the materials present in a specific paint layer. Especially for the identification of mixtures, it is difficult to draw a conclusion solely based on XRF analysis. Using SEM/EDX cross-sections, the specimen can be analyzed layer by layer, revealing even individual pigment grains. However, based on the results of element analysis (XRF, SEM/EDX) a clear identification of the pigments could not be achieved and compound specific analysis, by means of XRD and Raman spectroscopy, were used according to the available amount of the sample. For the investigation of the binding media as well as for the consolidation materials from previous conservation interventions, Py-GC-MS was applied. The strategy for this investigation was to get as much information as possible by using the minimum amount of original sample material. By Py-GC-MS a high amount of information can be obtained, due to its high sensitivity, especially for the identification of polymers [32].

The wall painting samples

In order to investigate the materials in the wall painting, seventeen paint samples from different areas (colors) were taken, for the characterization of the pigments and the binding media (about 1-2 mg), and five samples (labeled as DZS A-E, see table 1) were taken from the consolidation areas on the surface of the wall painting.

Instruments and parameters

For XRF analysis we used an instrument made by Tracor, USA (Spectrace 5000). The tube voltage and current were set to 30 kV and 0.02 mA, respectively. The measurements were carried out in air and the live time for each spectrum was 100 s.

The instrument used for SEM/EDX analysis was a Quanta 200 MK2 made by FEI Company, with an EDX detector made by AMETEK, USA. Five paint samples of the Dazhao Temple were selected for these investigations. The samples were embedded in synthetic resin to make polished cross-sections for the analysis. The cross-sections were investigated by means of optical and UV-fluorescence microscopy, with a microscope, type Orthoplan, Leitz, Germany, prior to the SEM/EDX analysis.

For XRD analysis, an instrument made by Rigaku, Japan (type RINT 2000) was used. Cu-K alpha radiation was employed at 40 kV and a tube current of 40 mA. The scan range ($2\theta/\theta$) was $5\sim60^{o}$.

For Raman spectroscopy analysis, an instrument LabRAM Aramis with a microscope device, Horiba Jobin Yvon, France was used. The parameters chosen for the investigation were: laser-633 nm, laser power-12.5 mW/1000, hole-1000 μm, slit-100 μm, grid-600, microscope Olympus 100x/0.9. The measuring time was 10 s with a CCD-camera as detector.

The identification of the organic components was carried out using Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS). A double shot pyrolyzer, type PY-2010iD, made by Frontier Lab, Japan, and a gas chromatograph mass spectrometer, GC-MS-QP2010 Plus made by Shimadzu, 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 was set to 250 °C. A capillary column SLB-5MS (5% diphenyl / 95% dimethyl siloxane), 0.25 mm internal diameter, 0.25 μm film thickness and 30 m length [Supelco] was used in order to provide an adequate separation of the components. The chromatographic conditions were as follows: The oven initial temperature was set to 40 °C for five minutes, followed by a gradient of 6 °C per minute up to 292 °C, for three minutes. The carrier gas 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 1:100 ratios. Ions were generated by electron ionization (70 eV) in the ionization

chamber of the mass spectrometer. The mass spectrometer was set from m/z 50 to 750, with a cycle time of 0.5 seconds. EI mass spectra were acquired by total ion monitoring mode. The temperatures of the interface and the source were 280 °C and 200 °C, respectively. NIST 05 and NIST 05s Library of Mass Spectra were available for the identification of the compounds. This method was applied according to the procedure described in [30] and slightly modified, which was optimized with reference materials of PVA and acrylic resin.

We should mention that no special sample preparation was necessary for the Py-GC-MS analysis. Small amounts of samples (about 0.2 mg) were put into sample cups and the specimens were dropped from the auto sampler directly into the Frontier Lab pyrolyzer. After pyrolysis the gas mixture was analyzed by GC-MS.

Results and discussion

The structure of the wall paintings and the pigments used

The images of the cross-section of the specimens (DZS 4, 6, 7, 12, 13, 17) are presented to reveal the structure of the wall painting (figure 2a-f). It is obvious, apart from sample DZS6, that all the samples have a thin paint layer, a white, finely grained preparation layer underneath and the bottom – the coarse ground layer (plaster). This 3-layer structure (paint layer, preparation and plaster) can also be visualized in the SEM. The images in figure 3 (fig.3a-f) depict the cross-sections of the specimens DZS 4, 6, 7, 12 and 17, where the morphology of the pigments and ground materials are also clearly visible, especially the typical grain shape of potash-lime-silica glass (smalt) shown in figure 3a. The pigment grains in the paint, preparation and ground layers could be analyzed individually by EDX point/area analysis, as marked in the images.

The results of the energy dispersive analysis in the SEM, as well as in the XRF are summarized in tables 1 and 2, where the color and the elements determined are listed in the first 2 columns.

Table 1. List of samples taken from the wall painting of the Dazhao Temple in Hohhot, Inner Mongolia, their colour and the results obtained by XRF, SEM/EDX and XRD.

Sample	Colour	Elements determined by XRF	Pigments identified
DZS 1	Red	Hg, (Ca, Fe, Cu), Pb	Cinnabar
DZS 2	Red	Si, Ca, Fe, (Ti, Sr)	Ochre
DZS 3	Red	Hg, (Ca, Fe, Cu), Pb	Cinnabar
DZS 4	Blue	Si, K (Ca), Fe, Co, Ni, As, (Sr)	Smalt
DZS 5	Only ground	-	-
DZS 6	Grey	-	Carbon black mixed with dolomite and alumo-silicate
DZS 7	Green	Cl, Cu, (Fe, Ca)	Mixture of atacamite/para-atacamite with alumo-silicate
DZS 8	Green	Cl, Cu, (Fe, Ca)	Same as DZS7
DZS 9	Green	Cl, Cu, (Fe, Ca)	Same as DZS7
DZS 10	White	Pb, (Ca, Fe)	Lead white
DZS 11	White	Pb, (Ca, Fe)	Lead white
DZS 12	Orange	Pb, Ca, (P, Fe, Sr)	Mixture of minium (lead oxide) with chalk
DZS 13	Yellow	As, S, Si, Ca, Fe, (Sr)	Orpiment with chalk (?)
DZS 14	Yellow	As, S, Si, Ca, Fe, (Sr)	Same as DZS13
DZS 15	Pink	Hg, Pb, Fe, Ca, (Ti, Cu, Sr)	Cinnabar and lead white
DZS 16	Flesh	As, S, Si, Fe,(Ca, Cu, Ti, Sr)	Orpiment and ocher
DZS17	Black/grey	-	Mixture of lead white, alumo-silicate and carbon black
DZS A-E	Consolidatant	-	-

Note: The elements underlined are present as main constituents and are used for the identification of the pigments, whereas the elements listed in brackets are minor or trace components; - was not analyzed by XRF, the results discussed in the text are based on SEM/EDX analysis

According to these elemental analyses, most of the pigments in the samples could be identified (column 4 in table 1 and column 3 in table 2). However, as XRF was carried out in air, where the elements with low atomic numbers such as Na, Mg, Al or Si can hardly or not at all be detected, due to the absorption of the low energy of the characteristic x-ray radiation, XRD was also applied for the identification of the crystalline structure of the chemical compounds present in various paint layers, especially for the green pigment in sample DZS 7 and the compounds in the ground layer presented in the figures 4 and 5, respectively.

The results of all these investigations (XRF, SEM/EDX and XRD) clearly reveal that for the ground layer a mixture of coarse sand (SiO_2) with fine grained alumosilicate was used. By SEM/EDX only silicon (e.g. Figs. 3a-3e) was detected in the big grains, whereas in the spectra of the fine grained components, Si with Na, Mg, Al, Ca and Fe was found. A more detailed conclusion can be drawn from the XRD analysis, where an evaluation of the diffractographs, using the reference database of JCPDS, reveals that, in addition to quartz, also calcite, mica, anorthite and estatit are present in the ground layer (Fig. 5). In the white fine preparation layer of the samples, elements including Mg, Al, Si, Ca and Fe were detected, indicating that dolomite and alumosilicate were the materials in the preparation layer.

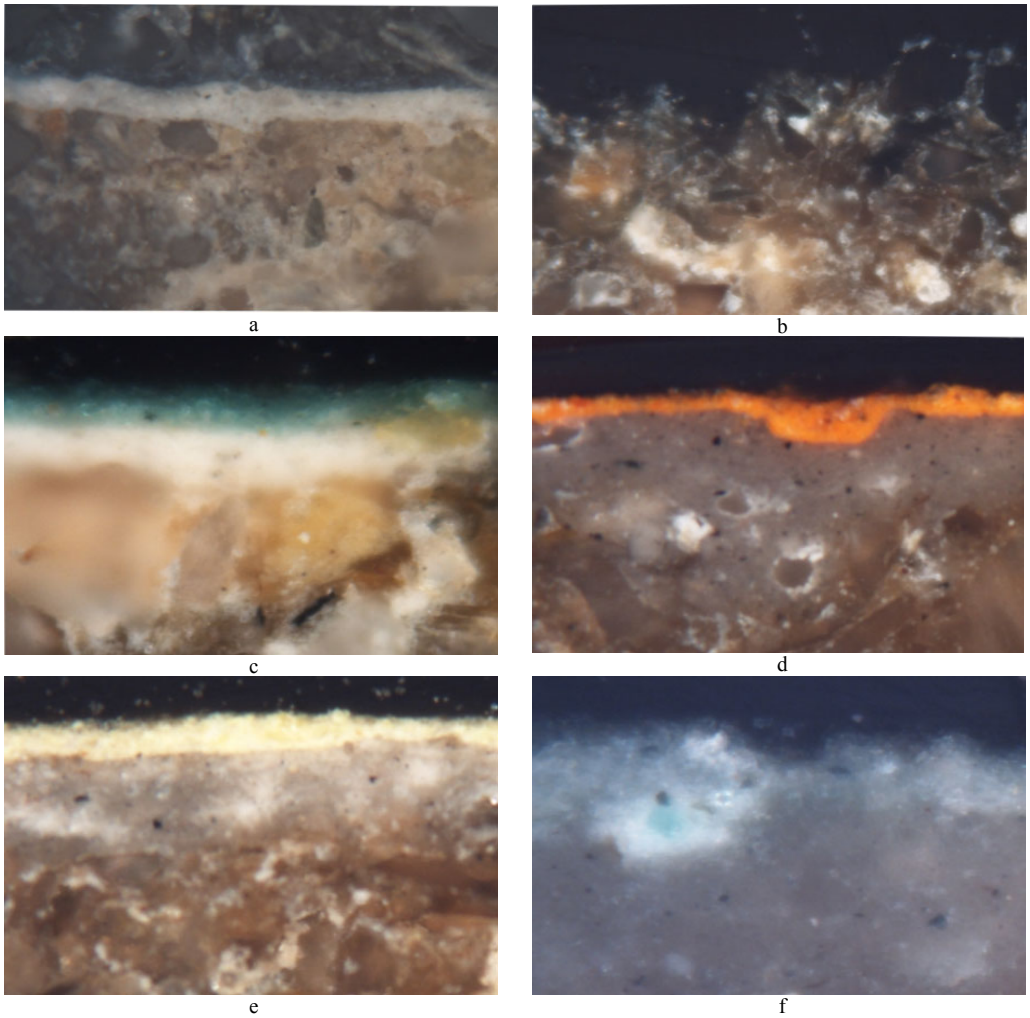

Fig. 2. Micrographs of the specimens:
a - DZS 4, b - DZS 6, c - DZS 7, d - DZS 12 , e - DZS 13, f - DZS 17.

For the bright red color in the wall painting, the pigment cinnabar (HgS) was used. That was determined by XRF, where due to the coincidence of the Hg M-lines (energy = 2.2 keV) with the S K-lines (energy = 2.3 keV) only Hg is listed in the table. For the less bright red areas in the wall painting red ochre (sample DZS 2) was applied. The sample DZS 4 taken from a blue area shows the elements typical for smalt in the XRF spectrum, as well as in the SEM/EDX.

The green areas where painted using the Cu-chlorides atacamite and para-atacamite, as resulted from the XRF (specimen DZS 7 – 9) as well as from SEM/EDX (Fig. 3c) analyses and it was confirmed by XRD (Fig. 4). Such a mixture of the green copper pigments was found in the Tang Dynasty wall paintings of Dunhang Grottos [33]. The white pigment (specimen DZS 10 and 11) was identified as lead white, by XRF. As for the yellow color (specimen DZS 13 and 14), it was difficult to conclude whether it was orpiment or para-realgar, solely based on the element analysis results (As and S were detected). Therefore, Raman spectroscopy was performed (Fig. 6). As strong and medium-intensity bands can be observed in the spectrum, at 154, 292 and 353 cm^{-1}, the presence of orpiment confirmed [34]. The gray color (specimen DZS 6 and 17, Fig. 3b, 3e and 3f) was achieved by mixing carbon black with lead white and small amounts of alumosilicate; the flesh tone (DZS 16) was obtained by a mixture of orpiment and ochre, whereas the pink color (DZS 15) contained cinnabar, lead white and probably small amounts of ochre too. Orange (DZS 12, Fig. 2d) was achieved using minium (Pb oxide) with chalk and alumosilicate.

Table 2. The results of SEM/EDX analysis of the five wall painting samples from the Dazhao Temple. The micrographs of the cross-section are shown in the figures 3a-f.

Sample Colour	**Elements found in paint layer or pigment grain**	**Materials in the paint layers**
DZS 4, Blue (Fig. 3a)	Particle 1: **Na, Si, K, Co, As** Area 2: **Mg, Al, Si, Ca, Fe** Particle 3: **Si**	Smalt Dolomite + alumosilicate Quartz
DZS 6, Grey (Fig. 3b)	Particle 1 and 3: **Na, Mg, Al, Si,** K, Fe Particle 2: **C**	Carbon black mixed with dolomite and alumo-silicate
DZS 7, Green (Fig. 3c)	Particle 1: **Cu, Cl** Particle 2: Al, **Si**, Cu, Cl, Ca Particle 3: **Mg, Al, Si, Ca, Fe** Particle 4: **Si**	Mixture of atacamite and para-atacamite with alumo-silicate Dolomite + alumosilicate Quartz
DZS 12, Orange (Fig. 3d)	Particle 1 and 2: **Si** Area 3: **Mg, Al, Si, Ca, Fe** Particle 4: Mg, Al**, Pb**,Ca Particle 5: **Ca,** Pb, C	Quartz Dolomite + alumosilicate Mixture of minium (lead oxide) with chalk
DZS 17, Black/grey (Fig. 3e and Fig. 3f)	Area 1: Al**, Si,** K, **Pb**, Ca, Fe Particle 1a**: Si,** Particle 1b: **C**, (Al, Si, Pb, Ca) Area 2: **Mg, Al, Si, Ca, Fe** Particle 3: **Si**	Mixture of lead white, alumo-silicate, small quartz grains and carbon black Dolomite + alumosilicate Quartz

Note: The elements printed in bolt are present as main constituents and are used for the identification of the pigments, whereas the elements listed in brackets are minor or trace constitutes.

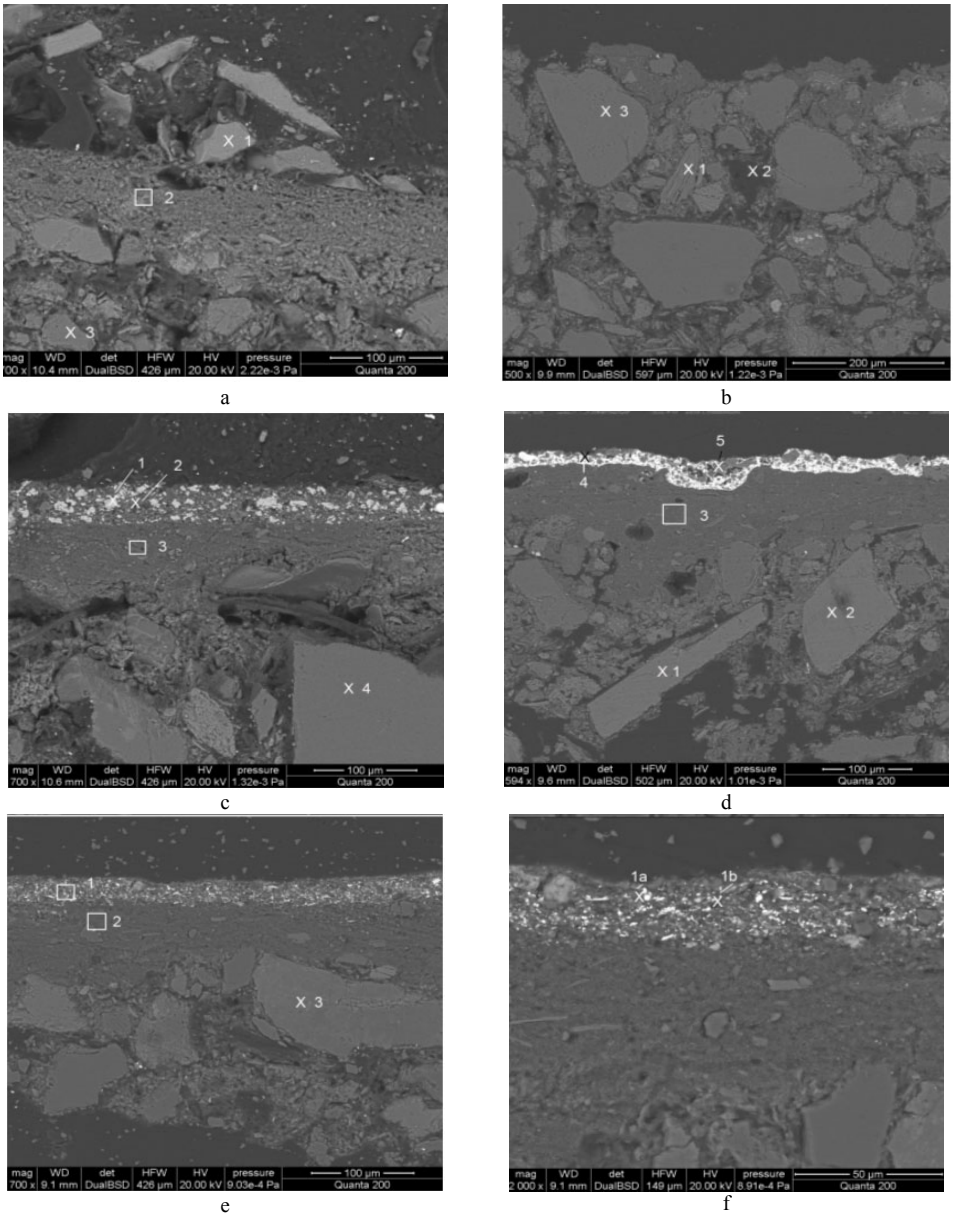

Fig. 3. SEM-micrograph of the specimens:
a - DZS 4, b - DZS 6, c - DZS 7, d - DZS 12 , e - DZS 17 , f - DZS 17 in larger scale; Those images show the coarse grains in the ground layer, the fine grained preparation layer and the bright pigment grains of the painted layer; the numbers marked in the images (1-5) were analyzed individually by EDX point/area analysis, as shown in table 2

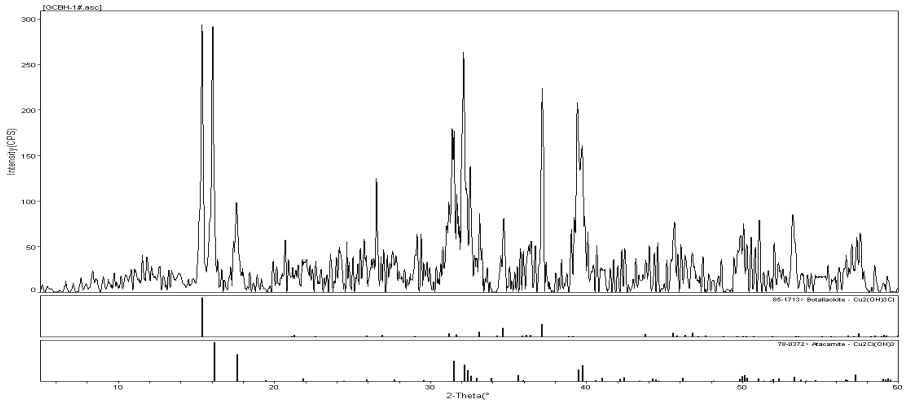

Fig. 4. XRD analysis of sample DZS 7 (green pigment) with the reference diffractograms of atacamite and para-atacamite

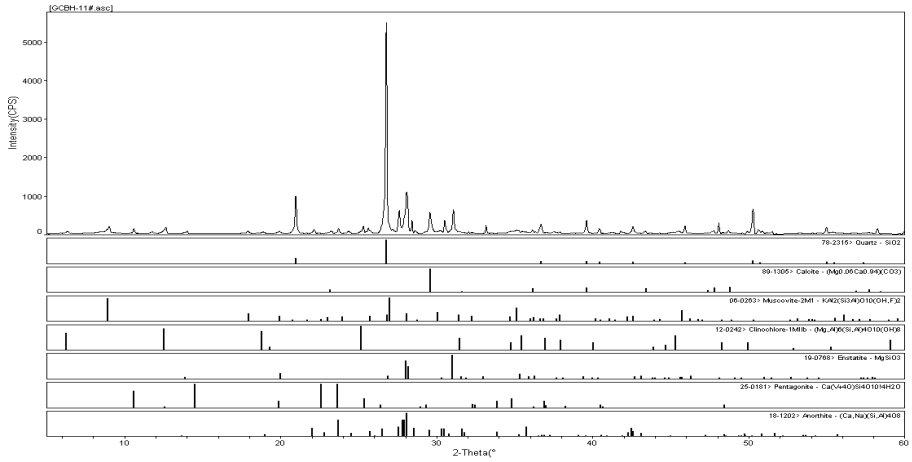

Fig. 5. XRD of a sample from the ground layer with reference diffractograms of JCPDS. Quartz, calcite, mica, anorthite and enstatit were identified.

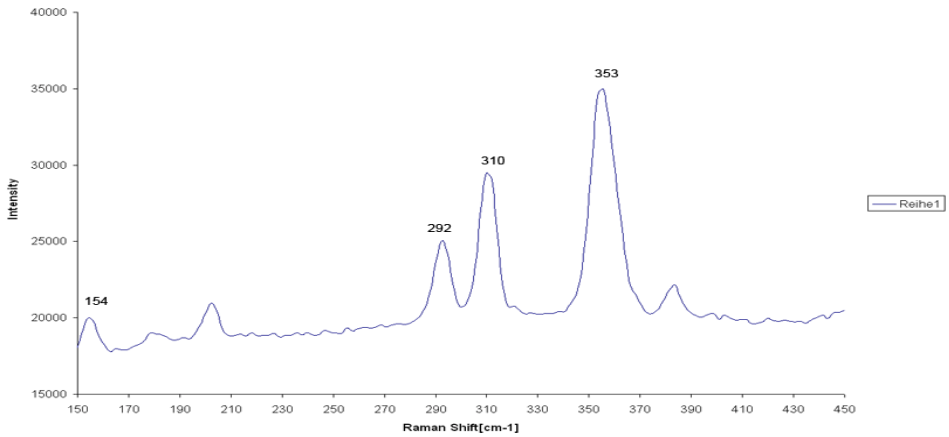

Fig. 6. Raman microscope spectra of yellow paint specimen (DZS13)

Identification of proteinaceous materials by Py-GC-MS

Ten of the samples with different colors were taken carefully with a scalpel (to minimize the preparation layer) and analyzed by Py-GC-MS techniques. Reference materials, including bone glue, egg and casein were analyzed by using the same Py-GC-MS parameters as the samples. The chromatographs of all the samples obtained by Py-GC-MS analysis are almost identical, so only one of the results is depicted in figure 7, the total ion chromatograph (TIC) of sample DZS 6. The compounds identified are listed in table 3. The marker pyrolysis products for animal glue, including pyrrole (m/z 67), 3-methyl-1H-pyrrole hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione (m/z 154), 1H-isoindole-1,3(2H)-dione and toluene were detected in the samples. By comparison to the reference material of animal glue, it can be concluded that animal glue is present in all the ten samples, which is in agreement with specialized publications [35-37]. In addition, two samples were taken from the preparation layer and analyzed using the same parameters as for the paint samples. No marker pyrolysis compounds were found, indicating that no binding media was used in the preparation layer.

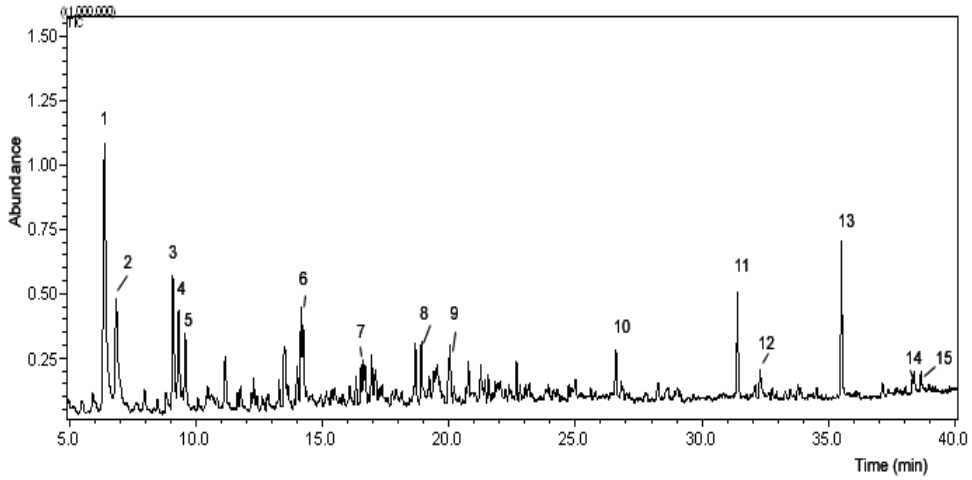

Fig. 7. TIC of sample DZS 6 obtained by Py-GC-MS analysis, compounds identified are listed in table 3

Table 3. The compounds identified in sample DZS6 by Py-GC-MS

Peak No.	RT	Area %	Compound identified
1	6.38	29.2	Pyrrole
2	6.85	8.6	Toluene
3	9.09	12.4	Furfural
4	9.31	8.6	3-methyl-1H-pyrrole
5	9.58	6.2	2-methyl-1H-pyrrole
6	14.23	4.9	Benzonitrile
7	16.62	2.7	1-(1H-pyrrol-2-yl)-ethanone
8	18.91	3.0	1H-pyrrole-2-carbonitrile
9	20.04	3.2	Azulene
10	26.60	2.9	1H-isoindole-1,3(2H)-dione
11	31.41	5.9	Benzofuro[3.2-d]pyrimidin-4(3H)-one
12	32.30	2.4	Hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione
13	35.51	8.3	Phthalic acid butyl undecyl ester
14	38.38	0.6	Oleic acid
15	38.66	1.0	Stearic acid

The identification of consolidation materials used in the painting by Py-GC-MS

As shown in figure 1b, the consolidant from the back side of the painting, which was used in the previous conservation process, emerged to the surface. In order to identify their composition, five samples taken from the conservation intervention areas (DZS A-E) were subjected to Py-GC-MS analysis. The chromatographs of the five samples obtained by Py-GC-MS are similar. The dominant peak in the chromatographs is phthalic anhydride (RT 23.44 min), which indicates that alkyd resins are present in the five samples. For all alkyd resin, phthalic anhydride was the main peak detected by pyrolysis and was, therefore, used as the diagnostic peak for alkyd resin [36]. One of the chromatographs is shown in figure 8. Styrene and vinyl toluene were also detected in the chromatograph. They are the co-polymers of alkyd, since alkyds were often modified with these compounds, to improve certain properties [38]. Dibutyl phthalate and dipropyl phthalate are the plasticizers normally used in alkyds for desired flexibility and durability.

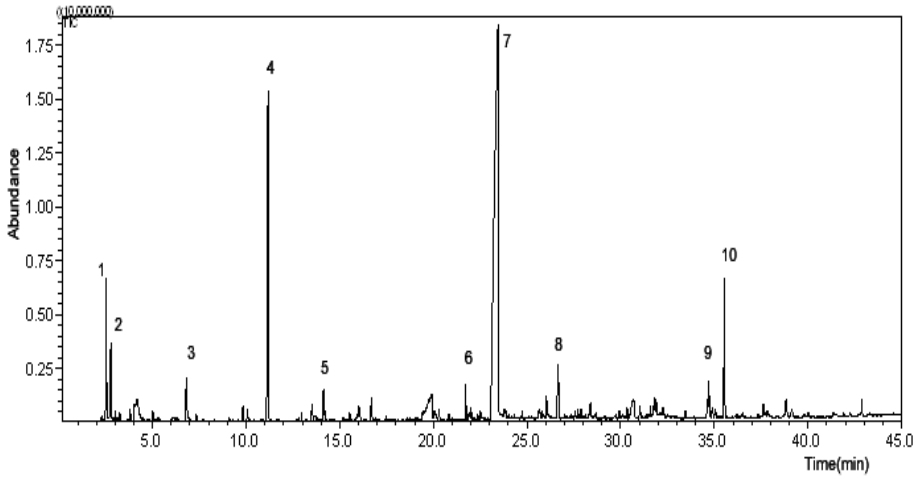

Fig. 8. TIC of sample DZS-D obtained by Py-GC-MS analysis; 1: propanal, 2: 2-propen-1-ol , 3: toluene, 4: styrene, 5: vinyl toluene, 6: benzoic acid 2-propenyl ester, 7: Phtalic anhydride, 8: 2-(hydroxymethyl)-1H-isoindole-1,3(2H)-dione, 9: dipropyl phthalate, 10: dibutyl phthalate

Conclusions

In this study, the painting technique, the pigments and the binding media, as well as the conservation intervention material used in the mural painting of Dazhao Temple in Inner Mongolia, were characterized. The painting was made in three layers: the first layer is the ground layer (plaster layer), made of local clay containing calcite with quartz, above it is a fine preparation layer made of dolomite with alumosilicate and on top is the paint layer. This is a very typical Chinese wall painting technique.

Orpiment, cinnabar, ochre, atacamite/para-atacamite, minium were the common pigments used in China of the 14th to 17th century, and they were also found in the wall paintings of the Dunhuang grottoes [39]. Additional mixtures of different pigments were identified in this painting, which were applied to achieve special color tones, such as the orange color (minium with chalk) and the gray color (lead white with carbon black). Previous studies

do not contain information about the use of smalt in paintings as early as those from the Ming Dynasty. The blue pigments identified in the wall paintings of the Dunhuang grottoes are Lapis lazuli, and azurite from the Sixteen States to the Qing Dynasty [37]. Only recently was smalt reported in the decorative paintings in the Qing Dynasty palace [40]. It is not clear when smalt was imported to China. The earliest use of smalt in China was reported in ceramics, where it was used for to achieve the blue and white pattern typical for the Yuan Dynasty [41]. Further research needed to determine whether the smalt is original or a later intervention material. It came as no surprise that animal glue was identified as a binding medium. It was also found in other Chinese wall paintings [30, 31]. The conservation materials used in Chinese wall paintings, PVAc, epoxy, shellac and gelatine were mentioned as consolidants in previous publications [27-29]. However, in the wall painting of the Dazhao Temple, different consolidation materials were found, such as the copolymer of alkyds with styrene and vinyl toluene.

Acknowledgements

This study is part of the project Rescue and Conserve the Endangered Wall Paintings in Museums of China, performed in cooperation between the Institute of Natural Sciences and Technology in Art, Academy of Fine Arts in Vienna (AFA) and the Chinese Academy of Cultural Heritage (CACH). We would like to thank for the support from the director of CACH, Zhang Tinghao, and the colleagues Cheng Qian, Dr. Sun Yanzhong and Dr. Dubravka Jembrih-Simbürger and Dr. Song Yan. The studied wall painting of the Dazhao temple was from the Hohhot Museum, China.

References

[1] C. Neelmeijer, I. Brissaud, T. Calligaro, G. Demortier, A. Hautojärvi, M. Mäder, L. Martinot, M. Schreiner, T. Tuurnala, G. Weber, *Paintings – a challenge for XRF and PIXE analysis*, **X-Ray Spectrometry, 29**, 2000, pp. 101-110.

[2] V. Janssens, *X-ray based methods of analysis,* **Non-destructive microanalysis of cultural heritage materials** (eds. K. Janssens, R. Van Grieken), Elsevier, 2004, 129-226.

[3] T. Turnala, A. Hautojärvi, *Examination of oil paintings by using a PIXE/PIGE combination*, **Nuclear Instruments and Methods B, 14,** 1986, p. 70.

[4] E. Manzano, A.G. Bueno, A. Gonzalez-Casado, M. del Olmo, *Mortars, pigments and binding media of wall paintings in the "Carrera del Darro" in Granada, Spain*, **Journal of Cultural Heritage, 1,** 2000, pp. 19-28.

[5] M. Schreiner, M. Melcher, M., K. Uhlir, *Scanning electron microscopy and energy dispersive analysis – applications in the field of cultural heritage*, **Journal of Analytical and Bioanalytical Chemistry, 387**, 2007, pp. 737-747.

[6] M. Mantler, M. Schreiner, F. Schweizer, *Museum: Art and Archaeology*, **Industrial Applications of X-Ray Diffraction** (eds. F.H. Chung, D.K. Smith), Marcel Dekker, Inc., New York, Basel, 2000, pp. 621-658.

[7] M. Sawczak, A. Kamińska, G. Rabczuk, M. Ferretti, R. Jendrzejewski, G. Śliwiński, *Complementary use of the Raman and XRF techniques for non-destructive analysis of historical paint layers*, **Applied Surface Science, 255,** 10, 2009, pp. 5542-5545.

[8] F. Cappitelli, F. Koussiaki, *THM-GCMS and FTIR for the investigation of paints in Picassos Still Life, Weeping Woman and Nude Woman in a Red Armchair from the Tate Collection, London*, **Journal of Analytical and Applied Pyrolysis, 75,** 2, 2006, pp. 200-204.

[9] M.R. Derrick, S. Dusan, J.M. Landry, *Infrared spectroscopy in conservation science. Book.* **Scientific tools for conservation**. The Getty Conservation Institute, Los Angeles, USA, 1999.

[10] J. Peris Vicente, J.V. Gimeno Adelantado, M.T. Doménech Carbó, R. Mateo Castro, F. Bosch Reig, *Identification of drying oils used in pictorial works of art by liquid chromatography of the 2-nitrophenylhydrazides derivatives of fatty acids*, **Talanta, 64**, 2, 2004, pp. 326-333.

[11] J. Peris Vicente, J.V. Gimeno Adelantado, M.T. Doménech Carbó, R. Mateo Castro, F. Bosch Reig, *Identification of lipid binders in old oil paintings by separation of 4-bromomethyl-7-methoxycoumarin derivatives of fatty acids by liquid chromatography with fluorescence detection*, **Journal of Chromatography A, 1076,** 1-2, 2005, pp. 44-50.

[12] J. Mills, R. White, *Analyses of paint media***, National Gallery Technical Bulletin, 1**, 1977, pp. 57-59.

[13] A. Andreotti, M. Bonaduce, M.P. Colombini, G. Gautier, F. Modugno, E. Ribechini, *Combined GC/MS analytical procedure for the characterization of glycerolipid, waxy, resinous, and proteinaceous materials in a unique paint microsample*, **Analytical chemistry, 78,** 13, 2006, pp. 4490-4500.

[14] I. Bonaduce, C. Blaensdorf, P. Dietemann, M.P. Colombini, *The binding media of the polychromy of Qin Shihuangs Terracotta Army*, **Journal of Cultural Heritage, 9**, 1, 2008, pp. 103-108.

[15] F. Caruso, S. Orecchio, M.G. Cicero, C. Di Stefano, *Gas chromatography–mass spectrometry characterization of the varnish and glue of an ancient 18th century double bass*, **Journal of Chromatography A, 1147**, 2, 2007, pp. 206-212.

[16] C. Marinach, M.-C. Papillon, C. Pepe, *Identification of binding media in works of art by gas chromatography–mass spectrometry*, **Journal of Cultural Heritage, 5**, 2, 2004, pp. 231-240.

[17] L. He, G. Liang, *Application of pyrolysis gas chromatography-mass spectrometry in the conservation and investigation of art objects*, **Wen Wu Bao Hu Yu Kao Gu Ke Xue, 15,** 1, 2003, pp. 55-60.

[18] G. Chiavari, N. Gandini, P. Russo, D. Fabbri, *Characterization of standard tempera painting layers containing proteinaceous binders by pyrolysis(/methylation) gas chromatography mass spectrometry*, **Chromatographia, 47,** 7-8, 1998, pp. 420-426.

[19] A. Piccirillo, D. Scalarone, O. Chiantore, *Comparison between off-line and on-line derivatisation methods in the characterization of siccative oils in paint media*, **Journal of Analytical and Applied Pyrolysis, 74**, 2005, pp. 33–38.

[20] L. Osete-Cortina, M.T. Doménech-Carbó, *Characterization of acrylic resins used for restoration of artworks by pyrolysis-silylation-gas chromatography/mass spectrometry with hexamethyldisilazane*, **Journal of chromatography A, 1127**, 1-2, 2006, pp. 228-236.

[21] F. Capitelli, T. Learner, A. Cummings, **Proceedings of the 13th Triennial Meeting Rio de Janeiro, Pre-prints of the ICOM Committee for Conservation, 1**, 22–27 September, James & James, London, 2002, pp. 231–237.

[22] G. Chiavari, D. Fabbri, S. Prati, *Gas chromatographic–mass spectrometric analysis of*

products arising from pyrolysis of amino acids in the presence of hexamethyldisilazane, **Journal of Chromatography A, 922**, 1-2, 2001, pp. 235-241.

[23] Q. Chen, T. Sinkai, M. Inaba, R. Sugisita, G. Huang, *An analysis of pigments from Sung and Yuan Dynasty tomb wall paintings of Fujian Province in China,* **Bunkazai Hozon-Syuhuku Gakkaisi 41**, 1997, pp. 78-87.

[24] L. Van Valen, *The matter of chinese painting and the various materials and technical factors in chinese painting*, http://www.chinamatters.nl/home.html

[25] K.M. Garland, J.C. Rogers, *Paradise: To Intervene or Not? A Review of Some Past Conservation Approaches for the Treatment of Clay-Based Chinese Wall Paintings and a Set of Seventeenth-Century Chinese Gate Panels*, Proceeding of the **Conservation of Decorated Surfaces on Earthen Architecture,** The Getty Conservation Institute, Los Angeles, 2006, pp. 66-75.

[26] J. Twilley, K. Garland, *Painting materials and deterioration phenomena in a Yuan Dynasty wall painting***, Second Forbes Symposium**, Freer and Sackler Galleries, Smithsonian Institution, Washington, DC, September 2003.

[27] M. Yang, L. Guo, *Discussion about the method of detaching wall painting*, **Tang Mo Bi Hua**, Shaanxi History Museum, Sanqin Publisher, Xian, 2006, pp. 344-348.

[28] Q. Shen, *Several questions about conservation of the wall paintings from Tung tombs*, **Tang Mo Bi Hua**, Shaanxi History Museum, Sanqin Publisher, Xian, 2006, pp. 329-336.

[29] W. Wang, *The detaching and restoration of wall paintings from Tang Princess tomb*, **Tang Mo Bi Hua**, Shaanxi History Museum, Sanqin Publisher, Xian, 2006, pp. 402-407.

[30] B. Su., G. Chen, Z. Fan, *The application of a new synthesized desalination material on the treatment of salting damage wall paintings in Mogao Grottoes*, Proceeding of the **Second International Symposium of the Terracotta Army and Polychrome Cultural Relics Conservation and Research**, 23-27th March, 2009, pp. 249-264.

[31] S. Wei, M. Schreiner, H. Guo, Q. Ma, *The identification of the binding media used in the wall paintings of Tang Dynasty tombs and Dazhao Temple*, **Scientific and Technological Research on Cultural Heritage,** 7, 2008, pp. 15-24.

[32] T. Learner, *The analysis of synthetic paints by pyrolysis-gas chromatograohy-mass spectrometry (Py/GC/MS)*, **Studies in Conservation, 46**, 2001, pp. 225–241.

[33] Y. Fuan, X. Chen, Z. Li, Z. Hu, *Micro diffraction analysis of the rare green pigment botallackite in ancient wall paintings*, **Journal of Lanzhou University**, **40**, 5, 2004, pp. 1-6.

[34] A. Rosalie David, *Raman spectroscopic analysis of ancient Egyptian pigments*, **Archaeometry, 43,** 4, 2001, pp. 461-473.

[35] G. Chiavari, G. Lanterna, C. Luca, M. Matteini, S. Prati, I.C.A. Sandu, *Analysis of proteinaceous binders by in-situ pyrolysis and silylation*, **Chromatographia, 57,** 9/10, 2003, pp. 645-648.

[36] G. Chiavari, C. Galletti, *Pyrolysis-gas chromatography/mass spectrometry of amino acids*, **Journal of Analytical and Applied Pyrolysis, 24,** 2, 1992, pp. 123-137.

[37] S. Tsuge, H. Matsubara, *High-resolution pyrolysis-gas chromatography of proteins and related materials*, **Journal of Analytical and Applied Pyrolysis, 8**, 1985, pp. 49-64.

[38] T. Learner, *Modern paints*, **Scientific examination of art**: **modern techniques in conservation and analysis**, National Academy of Sciences, Washington, DC, March 19-21, 2003. National Academies Press, 2005, pp. 137-151.

[39] Z. Li, *The analysis of the pigments in Tang dynasty wall paintings*, **Tang Mo Bi Hua**, Shaanxi History Museum, Sanqin Publisher, Xian, 2006, pp. 360-372.

[40] Y. Lei, L. Qu, X. Cheng, H. Yang, H., S. Wang, *The discovery of smalt in Jianfu Palace in Forbidencity*, **Proceeding the Second International Symposium of the Terracotta Army and Polychrome Cultural Relics Conservation and Research**, Xian, China, 23rd - 27th March, 2009, pp. 387-372.

[41] Q. Jiang, *Over the world- the attractive of blue white patterned ceramic* http://qkzz.net/magazine/0257-019X/2004/08/110204_2.htm

Received: June 1, 2010
Accepted: June 14, 2010