Tibetan Wall Paintings in Nako – behind the Scenes of Buddhist Artists' Craftsmanship

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The Buddhist temple complex at Nako in the remote Himalayan region in North India can be dated back to the period of its foundation at the end of the 11th and beginning of the 12th century. Inside four earthen temples, there is the earliest artistic heritage of the Tibetan Buddhism preserved in the form of mural paintings, polychrome clay sculptures, decorated wooden elements and ceiling panels. Due to its artistic qualities, the temple complex has become one of the most important and unique art works of its kind in the world.

From 2004 till 2010 staff members, students and alumni of the Institute of Conservation at the University of Applied Arts in Vienna worked within a research and conservation project on preservation of cultural heritage of the temple complex under the leadership of Prof. Dr. Gabriela Krist, the head of the Institute. The research was not only meant to perform an assessment of the materials used in 12th century in the Tibetan art, but also aimed to facilitate the work of art historians and guide conservators/restores during the conservation treatments. One of the key questions was to reveal the painting technique used in original 12th-century wall paintings, in particular the detection of the binding media of both grounds and paint layers.

The technical study was conducted by the coupling of various methods in co-operation of the Institute of Conservation, University of Applied Arts Vienna, the Conservation Science Department, Kunsthistorisches Museum Vienna and the Royal Institute for Cultural Heritage in Brussels. The results obtained delivered a comprehensive picture of the painting technique and materials of the original wall paintings. In particular, this presentation is focused on GC-MS and LC-MS/MS instrumentations, which revealed the proteinaceous binding material applied and even indicated a possible animal source of the proteins – the glue tempera based on bovine (or genetically close relative) glue – used in original murals.

1. Nako location
2. Nako village
3. Nako Temple complex
4. Original wall painting on the south wall of the Main Temple

Different methods of the binding media identification

SPOT TESTS

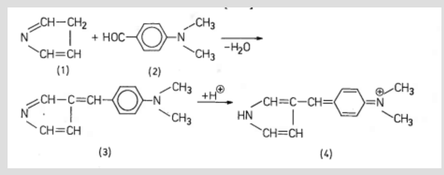
Altogether, there were undertaken spot tests on fifteen samples – eight on the samples of ground and eight on the samples of paint layers.

Microchemical test for proteins is based on detection of pyrrole-derivatives with p-dimethylaminobenzaldehyde.

Reference: Schramm, H.P. & Hering, B., 1995, Historische Malmaterialien und ihre Identifizierung. Stuttgart., Ferdinand Enke Verlag.


Sampling place


Resulting red-violet coloration of the filter paper soaked with the solution of the dimethylamino-benzaldehyde after the heating of the sample



Note: (1) pyrrole, (2) p-dimethylaminobenzaldehyde, (3) Schiff base, (4) resulting red-violet coloration

Conclusion:

The spots tests on all selected samples gave positive results for proteinaceous binding media in both the ground and paint layers.

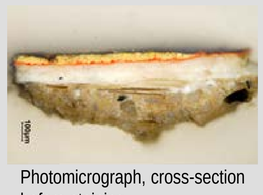
Due to the solubility of single layers, glue was expected to be used as the binding medium.

STAINING TESTS

Altogether, there were undertaken staining tests on cross-section prepared from twenty five samples. Staining of cross-sections was carried out with Ponceau Rot S in 1% CH_3COOH and Amidoschwarz AB 2.

Reference: Schramm, H.P. & Hering, B., 1995, Historische Malmaterialien und ihre Identifizierung. Stuttgart., Ferdinand Enke Verlag.
Martin, E., 1977, Some Improvements in Techniques of Analysis of Paint Media, Studies in Conservation 22, 63-67.


Sampling place


Photomicrograph, cross-section before staining


After staining with Ponceau S


After staining with Amido Black AB2

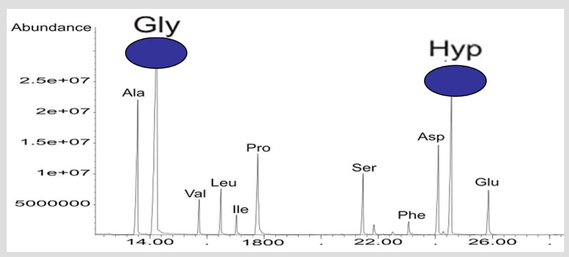
Conclusion:

The staining tests on cross-sections gave positive results for proteinaceous binding media in both the ground and paint layers and supported the results obtained by spot tests.

GC/MS

The analytical procedure is based on an acidic hydrolysis of proteins (100 µl 6M HCl at 105°C for 24h) to liberate amino acids, followed by the derivatisation and quantitative determination of amino acids as their silyl derivatives (15µl pyridine-pyridine hydrochloride + 30µl MTBSTFA at 60°C for 1h). Separation was performed on a DB-5 MS capillary column at temperature program 50°C (1min) to 320°C (12min) at $10^{o}C.min^{-1}$.


Sampling place



TIC chromatogram of paint layer sample.
Note: amino acids from animal glue (Ala=alanine, Gly=glycine, Val=valine, Leu=leucine, Pro=proline, Ser=serine, Phe=phenylalanine, Asp=aspartic acid, Hyp=hydroxyproline, Glu=glutamic acid

Conclusion:

GC-MS fully supported the preliminary spot and staining tests confirming the presence of proteins. According to the quantitative analyses of amino acids, chromatographic profile with high abundance of glycine and the presence of hydroxyproline proved the animal glue as a major binding medium in both ground and paint layers.

HPLC-MS/MS

Dissolution Denaturation	Reduction	Alkylation	Digestion	Sample clean-up	Redissolution	Nano-HPLC
5 M urea 2 M thiourea 0.7% SDS 50 mM Tris sonification	*10 mM DTT 60°C ; 60 min*	*10 mM IAA 27°C ; 15 min*	*Dilution (10x ; 50 mM Tris) 0.2 ng/µL trypsin 37°C ; overnight*	*evaporation to dryness solid phase extraction*	*evaporation to dryness 0.1 M formic acid*	**Nano-ESI-QTof-MS/MS**

Sample preparation in steps


Sampling place

Sample Nr	Number of peptides			Result
	COL1A1	COL1A2	COL3A1	
G43	9	7	1	animal glue (probably bovine glue)
L85	6	2	1	animal glue (probably bovine glue)
L128	20	16	2	animal glue (probably bovine glue)
K56	11	1	0	animal glue (probably bovine glue)

Results of the SwissProt library search

Coll 1A1 sequences of bovine species

Conclusion:

Protein analyses revealed the presence of animal glue. The highest similarity was achieved with bovine collagen sequence, which indicates a bovine (or a genetically close relative) source of the glue. However, it was impossible to distinguish between cow- and yak-based glues. This was caused by the lack of trustworthy yak glue reference material and to the relatively low number of identified collagen peptides in the sample.

DNA analysis

One sample underwent the mitochondrial DNA (mtDNA) testing; the obtained sequences should be compared with the mitochondrial sequences of the genuine Himalayan yak.


Sampling place

Isolation of DNA of animal glue from wall painting


Himalayan yak – illustration of the "source" for the reference DNA

Conclusion:

The identification of the species was applying molecular genetic methods, but unsuccessfully. The samples of original material were too small to allow the sufficient material isolation and thus also precise species identification.

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