ON THE TECHNOLOGY OF CENTRAL ASIAN WALL PAINTINGS: THE PROBLEM OF BINDING MEDIA

V. J. BIRSTEIN

Abstract—Organic components of paint layers and grounds in specimens of late antique and early medieval Central Asian wall paintings were studied. Quantitative analysis of amino acids isolated from specimens of Mansur-Depe wall paintings, second to first century B.C., has demonstrated that gelatin was used for the preparation of painting media and grounds—proline, glycine and alanine were revealed to a high percentage while hydroxyproline was not detected. In other wall paintings of the second to the eighth century the use of plant gums was inferred since polysaccharides isolated from the specimens had infrared spectra resembling those of polysaccharides from the *Prunoideae* sub-family. The gum used in the Toprak-Kala wall paintings, third to fourth century, and in a nineteenth-century painting from Khiva could be identified precisely: it was either apricot or cherry gum. The technique used for the preparation of paints and grounds in Mansur-Depe and Kara-Tepe, second to fourth century, resembles those described in medieval Indian manuscripts.

1. INTRODUCTION

During the last few decades many archaeological objects with monumental paintings dating back to antiquity and the early middle ages have been discovered in Central (Middle) Asia. Archaeologists, art experts and restorers who studied these paintings did not do any research on their binding media and grounds, believing that it is impossible to make experiments of this kind [1]. Yet, as was pointed out by R. de Silva [2], one can speculate about the technique of a monumental painting only after isolating and identifying the binding medium. Accordingly, in order to obtain an insight into the technique of Central Asian painters, we investigated specimens of paintings from a series of buildings dating back to different periods: the Parthian temple of Mansur-Depe, second to first century B.C. [3]; the Bactrian Buddhist temple complex of Kara-Tepe, second to fourth century [4]; the Khorezmian palace of Toprak-Kala, third to fourth century [5]; houses of Sogdian city nobles in Pendjikent, seventh to eighth century [6]; the Buddhist temple of Adjina-Tepa, seventh century [7]; and the Tashkhauli palace, 1830, in Khiva.

2. MATERIALS AND METHODS

Samples of Paintings

1 – From Mansur-Depe—small fragments with red paint on a relatively thick (2–3 mm) ground. The paint must have been made of Kzyl-kessak (a kind of ochre) as a pigment [3]. The ground consists of chalk with fillers: pounded ceramics and small pebbles [3]. It was placed on the mud plaster. The samples were collected in the portico (aiwan).

2 – From Kara-Tepe—fragments with red paintings and a fragment with a polychromatic painting from the P-II cave temple. The paintings are made on a ground 1·5–2·0 mm thick. The ground is different from that of Mansur-Depe. It is looser than the latter, almost insoluble in HCl, and with sand as the filler. The ground must have been spread in thin layers. The uppermost layer just below the painting is the finest and whitest one. The ground was placed over the sandstone walls of the cave.

3 – From Pendjikent—fragments of a thick clay plaster with fillers. A thin layer of white ground is over it. The colouring is black and brownish (the pigments are soot and ochre [8]).

4 – From Toprak-Kala—small fragments of paintings made in black paint over a red background. There is a thin layer of dense white ground under the paintings. The ground covers a thick mud plaster.
5 – From Adjina-Tepa—a fragment of a painting made with blue, pink and yellow paints (the pigments are ultramarine and ochre [7]) over a plaster ground 1·0–1·5 mm thick.
6 – A fragment* from Khiva—a piece of lime plaster (size 2 × 3 cm) with blue, black and brownish colouring.

Protein hydrolysis was carried out according to Stein and Moore [9]: 1–10 mg of a specimen were hydrolysed under vacuum (prior to hydrolysis the specimen was three times frozen under nitrogen and thawed under vacuum) for 24 h in 6 N HCl at 105°C. The hydrolysate was filtered through a G5 glass filter and concentrated in a vacuum rotating evaporator. In some cases, to achieve better purification, the hydrolysate was absorbed to a Dowex-50 column and the amino acids were eluted with 2 N NH_4OH. Salt-free amino acids were obtained by evaporation of the ammonia solution in a rotating evaporator.
Chromatography of protein hydrolysates and amino acid mixtures on 'Silufol UV_{254} Kavalier' slides was carried out in an n-butanol/acetate/water (60:20:20) system [10]. The chromatograms were dyed with 0·5% ninhydrin in ethanol.
Quantitative amino acid analysis was performed on a 'KLA-3B Hitachi' device. The conditions of the separation process were: (a) 0·9 × 50 cm column; 0·2 M sodium citrate buffer, pH 3·25–4·25; flow rates 60 mm per hour (buffer) and 20 mm per hour (dye); 55°C; (b) 0·6 × 10 cm column; 0·35 M sodium citrate buffer, pH 5·28; flow rates 60 mm per hour (buffer) and 30 mm per hour (dye).
Polysaccharide hydrolysis was carried out in 1 N H_2SO_4 for 10–12 h in a boiling water bath (1–5 mg sample) [11]. The hydrolysate obtained was neutralized with $BaCO_3$, and the $BaSO_4$ precipitate formed was removed by filtration. Some Dowex-50 × 8 in (H^+) form was added to the filtrate, the mixture was centrifuged, and the supernatant dried in a vacuum rotating evaporator.
Chromatography of polysaccharide hydrolysates was carried out as follows:
a – In preliminary experiments—on 'Silufol UV_{254}' slides in n-butanol/acetate/water (60:20:20) system.
b – In more precise experiments—on thin layers of microcrystallic cellulose (GDR) by three successive runs at 37°C in ethylacetate/pyridin/water (100:35:25) system [12]. Cellulose was spread over 4·5 × 20 cm glass plates (10 g cellulose were homogenized in 60 ml water). The chromatograms were developed with anilinephtalate reagent.
c – Gas chromatography of polysaccharide hydrolysates was performed on a 'Pye Argon'

*The quantity of sample used can be summarized as follows:

Wall painting	*Quantity of samples (g)*	*Quantity of isolated polysaccharides (mg)*
Mansur-Depe		
ground	2–3	—
paint layer	2	—
Kara-Tepe		
ground	1·5–2	2–3
paint layer	1	2–3
Pendjikent		
ground + paint layer	1	3–4
Toprak-Kala		
ground + paint layer	1	2
Adjina-Tepa		
ground + paint layer	1	2
Khiva	1	5

chromatograph. Prior to the analysis, monosaccharides in the hydrolysates were reduced to polyoles and transformed to acetylated derivatives [13] as follows: a dried neutralized hydrolysate was mixed with 10–15 mg of sodium borhydrate in methanol and kept for 1 h. The excess of borhydrate was removed by treating with KY-2 (H^+) cationite, the mixture was evaporated and dried several times by evaporation from methanol. The dry residue was treated for 4 h with a 1:1 mixture of acetanhydrid and pyridin. The separation was carried out in a 3% ECNSS-M on gas chrome Q column at 180°C. 5 ml of 20% specimen solution in chloroform was introduced and argon was used as a developer.

Infrared spectra were recorded on a 'Perkin-Elmer Model 257' IR spectrophotometer. Specimens were pressed into pellets with 150 mg of KBr powder.

3. RESULTS

In the first series of experiments fragments of Mansur-Depe wall paintings were studied. In preliminary analysis two specimens of the ground separated from the paint layer were hydrolysed in 6 N HCl and in 1 N H_2SO_4. De-salted and neutralized hydrolysates were subjected to chromatography on 'Silufol UV_{254}' slides. After dyeing with ninhydrin and anilinephtalate only amino acid spots could be observed, which implied that the ground contained protein. However, when a sample of the ground was dissolved in 1 N HCl, centrifuged, and the supernatant dialysed against water for 72 h, no polymer material was found in the dialysate. Instead, a mixture of amino acids was revealed in the residue obtained after evaporating the dialysis water. Obviously, the major part of the protein on the ground has disintegrated into amino acids.

To find out what kind of protein was used for the preparation of the binding medium, quantitative amino acid analysis was carried out. For this purpose a specimen of the ground was dissolved in 1 N HCl, and the solution was centrifuged and applied to a Dowex-50 × 2 column. The results of quantitative analysis of the amino acid mixture eluted from the column are presented in Table 1. For comparison, the amino acid composition of gelatin from an Italian painting of the fourteenth century reported by Keck and Peters [14] is also shown.

One can see that no hydroxyproline (whose content in collagen and gelatin is usually as high as 10–14%) was detected in the ground. However, high percentages of proline, glycine, alanine and glutamic acid revealed in the samples indicate that the ground did probably contain gelatin which had disintegrated into amino acids, while hydroxyproline, which is less stable than other amino acids [15, 16], might have degraded. In other words, one can conclude that a glue from collagen-rich animal tissues, such as skin and bones, was used as the binding medium for the ground.

Similarly, the amino acid mixture from the paint layer was isolated and purified. The data of Table 1 show that the amino acid composition of this mixture is similar to that in the ground. Hence we conclude that an animal glue was used as binding medium both for the paints and for the ground.

Next we studied the residue obtained after centrifugation of the initial suspension of the ground, with the expectation that not all gelatin had degraded into amino acids and some polypeptides might be trapped in the residue. The residue was hydrolysed and the chromatography of the hydrolysates on 'Silufol UV_{254}' slides revealed an amino acid mixture which resembled the one isolated from the solution by column chromatography. However, the amount of amino acids was too small to permit accurate analysis.

Specimens of the Kara-Tepe painting were analysed in the following way. Specimens of the ground or the paint layer were homogenized, boiled in water for 10 min, and the pellet obtained after centrifugation was successively treated with 1 N HCl and 1 N NaOH.

TABLE 1

AMINO ACID COMPOSITION OF MIXTURES ISOLATED FROM GROUND AND PAINT LAYERS OF A PAINTING FROM MANSUR-DEPE, AND OF GELATIN

	Ground M	mol %	*Paint layer* M	mol %	*Gelatin* (14) mol %
Hydroxyproline	—	—	—	—	4
Aspartic acid	0·0237	4·5	0·0834	6·7	6
Threonine	0·0109	2·1	0·0142	1·1	2
Serine	0·0310	6·1	0·0522	4·2	4
Glutamic acid	0·0730	14·4	0·1505	12·0	9
Proline	0·0370	7·3	0·1024	8·2	13
Glycine	0·0855	16·9	0·5180	41·5	34
Alanine	0·0642	12·7	0·1880	15·1	13
1/2 Cystine	traces	—	0·0290	2·3	—
Valine	0·0218	4·3	0·0312	2·5	2
Metionine	0·0060	1·2	0·0117	0·9	—
Isoleucine	0·0109	2·1	0·0118	0·9	2
Leucine	0·0340	6·7	0·0285	2·3	3
Tyrosine	0·0127	2·5	0·0155	1·2	—
Phenylalanine	0·0126	2·5	0·0131	1·1	2
Lysine	0·0397	7·8	—	—	2
Histidine	0·0440	8·7	—	—	5
Sum total	0·5060	100·0	1·2495	100·0	101

The solutions were pooled, the pH adjusted to neutral, and dialysis against water carried out. After evaporating the dialysate in a vacuum rotating evaporator, the infrared spectra of the residue were recorded. A similar technique of isolating binding media from wall paintings was earlier employed by Belgian authors [17, 18]. In all experiments a polysaccharide (usually with contaminating inorganic substances) was isolated.

Figure 1 shows two typical spectra of the substances obtained (A, B) which virtually completely coincide. There is a band of stretching vibrations of bound OH-groups at 3400 cm^{-1} and a band of stretching vibrations of CH-groups at 2800–3000 cm^{-1}. Both spectra show absorption at about 1740 cm^{-1} and 1640–1620 cm^{-1}. The former weak band could be due to stretching vibrations of C=O groups of non-ionized acids and the latter one to ionized carboxylic groups, i.e. to the salts of uronic acids [19, 20]. These distinct bands can usually be seen in the spectra of vacuum-dried solutions of gum polysaccharides [20 and our experiments]. Sometimes the band in the 1600 cm^{-1} region is attributed to absorption by water [17], but in our case it would rather be due to absorption of the native apricot gum (Fig. 1, G).

At 1400–1500 cm^{-1} there is a band representing deformation vibrations of CH groups. However, it should be noted that bands of COO^- groups may also be present in this region [19]. The difference between the two spectra in this region could be due to inorganic constituents of the specimens. Even 72 h of dialysis were sometimes insufficient for the complete removal of inorganic contamination. After burning down these substances, the band at 1000–1100 cm^{-1} shifted into the region of 1120–1150 cm^{-1}, and a band at 670 cm^{-1} appeared. These bands could be due to the presence of gypsum [21].

Chromatography of hydrolysates of substances isolated on cellulose thin layers revealed spots of xylose, mannose, glucose and glucuronic acid. The xylose spot was the most inten-

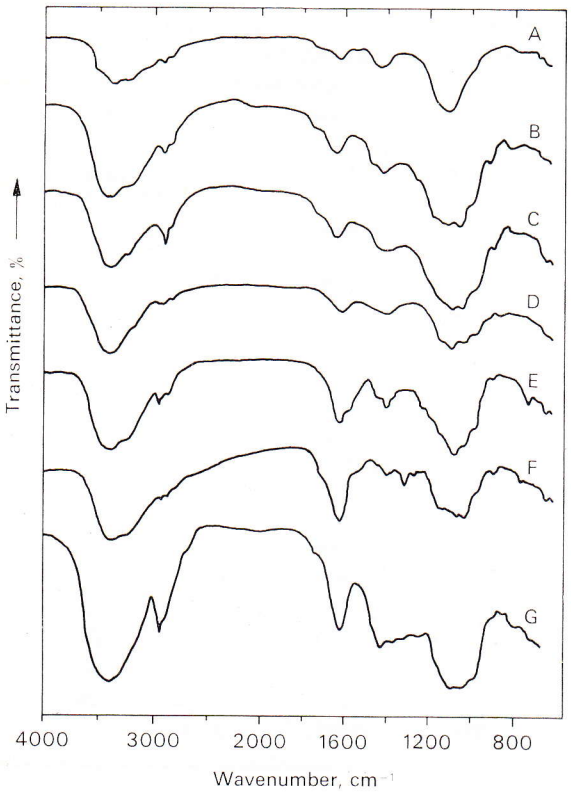

FIG. 1 Infrared spectra of substances isolated from: (A) red paint fragment from Kara-Tepe; (B) paint layer of a polychrome fragment from Kara-Tepe; (C) a sample from Pendjikent; (D) paint layer from Adjina-Tepa; (E) Toprak-Kala painting; (F) paint layer from a Khiva specimen and (G) of apricot gum.

sive, that of mannose was somewhat paler—the spots of the other sugars were barely visible. These results were confirmed by the data of gas-liquid chromatography of hydrolysates of a substance isolated from the paint layer of the polychrome fragment: it was possible to separate xylitol and mannitol while the alditol acetates of the other components were almost invisible. Hence both the paint and ground layers of Kara-Tepe contain a polysaccharide which includes the above-mentioned sugars. This implies that a glue prepared from plant gums was used as a binding medium. Unfortunately, from the components revealed it cannot be inferred, however approximately, what kind of plant gum was used for the preparation of the glue.

The same procedure was used for the isolation of the binding media from wall painting fragments from Pendjikent, Toprak-Kala, Adjina-Tepa and Khiva. With the specimens from Pendjikent and Toprak-Kala it was not possible to separate paint and ground layers, and they were extracted together. In the case of the Adjina-Tepa fragment the two layers were easily separated, so the binding media from ground and paint layers were analysed separately. Finally, only the paint layer was analysed in the case of the Khiva fragment.

As is evident from Figure 1, which shows infrared spectra of the isolated substances, the spectrum of the binding medium of Pendjikent specimens (Fig. 1, C) resembles remarkably that of Kara-Tepe paint layer samples (Fig. 1, B). This similarity was confirmed by the

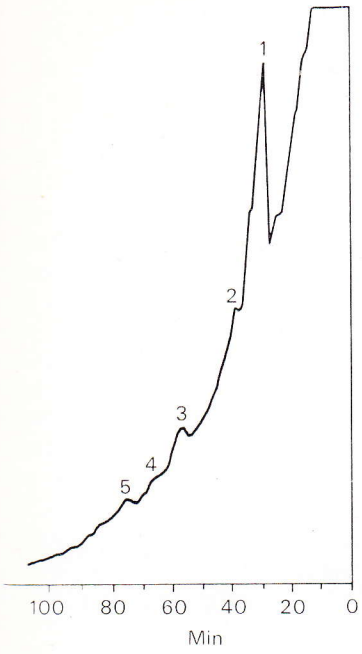

FIG. 2 Gas chromatographic separation of monosaccharide derivatives from a hydrolysate of the Pendjikent binding medium: (1) xylitol; (2) the derivative of glucuronic acid; (3) mannitol; (4) galactitol; (5) glucitol.

results of gas chromatography of polysaccharide hydrolysates (Fig. 2): the chromatograms of Pendjikent samples contained distinct peaks of the alditol acetates of the same major components xylose (1) and mannose (3). In addition, this polysaccharide contains glucuronic acid (2), galactose (4) and glucose (5) in considerable quantities. Consequently, gums from closely related but not identical plants were used in Pendjikent and Kara-Tepe. As can be seen from comparison of the spectra of the substance from the Adjina-Tepa paint layer (Fig. 1, D) with the spectra of other binding media and of apricot gum (Fig. 1, G), this substance is also a polysaccharide. The same spectrum was characteristic for the substance isolated from the ground of the painting. However, this polysaccharide is different from those revealed in fragments from Kara-Tepe and Pendjikent and does not resemble the polysaccharides of the fruit-tree gums. This conclusion was confirmed by the results of chromatography on cellulose thin layers: spots of xylose, mannose and glucose were detected, the latter being the most intensive. Unfortunately, it is impossible to name the plant whose gum was used for the preparation of the glue employed as the binding medium in this case.

IR-spectra of the components isolated from the specimens of paint and ground of Toprak-Kala (Fig. 1, E) and from the paint layer of Khiva (Fig. 1, F) are very similar; the differences in the regions of 1340 cm^{-1} and 1050–1250 cm^{-1} could probably be due to different levels of inorganic components. Both spectra are practically identical to those of fruit-tree gums, particularly to that of apricot (*Armeniaca vulgaris*) gum (Fig. 1, G). It should be emphasized that the spectra of gums from apricot, cherry (*Prunus cerasus*) and *Prunus avium* (the gums were collected in Tashkent) were virtually the same, which implies that the gums could not be distinguished on the basis of the spectra.

It is also difficult to distinguish the gums of cherry and apricot with the use of thin layer chromatography of hydrolysates since they contain almost the same set of monosaccharides. The identification of gums was possible only on gas-liquid chromatography of hydrolysates:

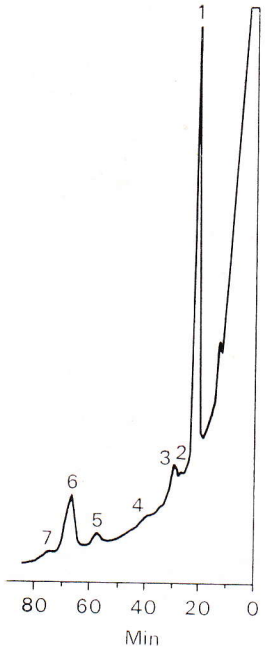

FIG. 3 Gas chromatographic separation of monosaccharide derivatives from a hydrolysate of apricot gum: (1) arabinitol; (2) rhamnitol; (3) xylitol; (4) the derivative of glucuronic acid; (5) mannitol; (6) galactitol; (7) glucitol.

in apricot gum the ratio of arabinose to galactose was approximately 3 to 1 (Fig. 3), in cherry gum 2·3 to 1 (the corresponding ratios reported by others are 1 to 1 and 1·2–2·6 to 1 [22, 23]).

Comparison of the spectra of isolated polysaccharides and gums shows that the former have more intensive bands at 1400–1420 cm^{-1} and 1620–1640 cm^{-1} and an additional band at 1240 cm^{-1} which could be explained by the presence of dissociated carboxyl groups [19] and inorganic components, respectively. Chromatography of polysaccharide hydrolysates revealed the following monosaccharides: galactose, xylose, traces of mannose and glucose and, probably, arabinose. These are normally to be found in the composition of apricot and cherry gums.

Thus, for the wall paintings in the Toprak-Kala and Khiva palaces, glues prepared from cherry and apricot gums were used as binding media. It should be emphasized that in Kara-Tepe and Pendjikent gums from a species of the *Prunoideae* sub-family were probably also used since xylose is known to be the main component in some *Prunoideae* gums.

4. DISCUSSION

We have shown that the ancient painters of Central Asia used both animal glue (Mansur-Depe) and plant glues (Kara-Tepe, Pendjikent, Adjina-Tepe, Toprak-Kala) as binding media. Since no definite terminology describing the technique of monumental wall painting exists, we should make it clear from the start that by glue paintings we shall mean those made with paints mixed with animal glue and gums, and by tempera paintings, those made with egg-yolk paints.

The bulk of the paintings of the Central Asian buildings of antiquity and the early medieval periods show the influence of Buddhist art (4; 6; 7), while the paintings of the former Buddhist temple complexes Kara-Tepe and Adjina-Tepa are examples of Buddhist paintings, the Kara-Tepe paintings being three to four centuries older than most of those in India.

That is why the knowledge of the technique of Indian monumental wall painting will help us to understand the painting technique of Central Asian masters.

Three main ancient sources dating back to the seventh, twelfth and sixteenth centuries, as well as some less famous ones, have survived which describe in detail the entire process of wall painting: preparation of walls, laying a ground, preparation of paints, drawing and painting [24–27]. The process differed basically from that of European fresco painting which seldom used natural binding organic components. The ground was made in the following way: lime or white clay was mixed with sand, soil, pounded ceramics, and a glue solution added. There were various kinds of glue: that of plants (among other things, masters used gums, pulps and saps of different plants and trees, broth of leguminous plants and bananas) and animal glue (gelatin produced by boiling buffalo skins) and even bees-wax. Once dried, the ground was covered with a thin layer of a mixture of clay or pounded shells with plant or animal glue. The same plant or animal glue was used as a binding medium for paints.

Studies of the paintings of Indian cave temples were started at the beginning of the twentieth century [2], but it was S. Paramasivan who carried out systematic research between 1930–40 (see, e.g., references 29–33). It was discovered that in almost all the buildings examined the ground consists of two layers: the lower, thicker (1·5–2·5 mm) one and the upper, thinner (0·6–0·8 mm) one. Chemical analysis showed that, usually, there is lime with an admixture of sand in the thick layer and only lime in the thin one. In most cases, no organic components were discovered in the paintings [28–31]. Only in the black pigments of some of the seventh- to ninth-century paintings was plant gum discovered [32, 34] as were traces of oil in the ninth- to fifteenth-century paintings. Of course, one cannot trust the results of this research completely since the methods used were not perfect. However, according to the recent review of O. Agrawal, there are no natural organic glues in a large number of Indian paintings [27]. That is why S. Paramasivan and O. Agrawal supposed that paintings had usually been made in the fresco secco technique, while lime water was used as a binding medium [27, 29–32, 34].

Buddhist cave temples of the early medieval period are also to be found in Chinese Turkestan and Afghanistan. According to S. M. Dudin's description of cave complexes in Eastern China published between 1910–20, paintings there were usually made on a ground consisting of lime and sand, or plaster. In the author's view, those are tempera paintings [35]. According to R. J. Gettens, who studied samples of paintings in two cave temples situated in Chinese Turkestan and Afghanistan, the painters had used mineral pigments mixed with animal glue, and used plaster for making the ground [36, 37]. These data also need confirmation. The discrepancy between the results of the experiments (the absence of a binding medium in most of the paintings) and the Indian manuscripts is all the more incomprehensible, because, according to modern traditional Eastern methods, glues are being used for wall paintings. For example, egg tempera was being used in China as recently as the beginning of this century [35], while glue made out of animal skins is still being used in Japan. In Central Asia, paintings on gypsum are made in mixed tempera: at first mineral pigments are mixed with apricot gum glue (i.e. apricot gum dissolved in water), and then egg yolk is added [38]. Sometimes painters use only apricot gum glue while mixing black pigment with egg yolk [38]. Cherry gum and a glue made out of the roots of the eremurus plant are also widely used in Central Asia [1]. Its glueing capacity is accounted for by eremuran and other polysaccharides present in the roots [39].

The fact that masters used egg yolk-based paints in Central Asia was demonstrated in 1927 by Professor N. N. Andreev using serological precipitation reactions [40]. Andreev obtained rabbit-blood serum from a rabbit which received injections of fresh egg yolk during one month. As experimental material he used fragments of medieval Tangut paintings of about the twelfth century, collected at Khara-Khoto in the Gobi desert, an ancient city destroyed

by the Mongols in the thirteenth century and rediscovered in the twentieth century. Painting samples of Russian ikons were used as controls. After layering of the serum over the solution of the binding medium extracted by alkali, a positive precipitation reaction was observed both in experimental and in control samples. Our experiments confirm the conclusion about the traditional use of cherry and apricot glues for Central Asian paintings for the case of a nineteenth-century specimen from Khiva.

Our data concerning the use of animal and plant glues as binding media in the monuments examined are well in accordance with the ancient and modern methods of Eastern painting. The technique of making ground and paints in Mansur-Depe resembles some of the methods described in Indian tracts, while the Kara-Tepe technique resembles other methods mentioned in the tracts. For instance, in Mansur-Depe the ground is made out of chalk with fillings (small pebbles and pounded ceramics) and gelatin glue, and paints are made out of pigments and the same glue. Indian tracts mention all these substances. The only difference is that here there is no fine thin ground layer, which was compulsory in Indian paintings. That is why one cannot agree with Koshelenko *et al.* [3]—who suppose that there is some similarity between the Mansur-Depe paintings and the Black Sea area frescoes, since in these cases a basically different technique was used: we have detected animal glue in the paint layer and the ground. In Kara-Tepe, sand and plant glue were added to the ground, and there is a thin fine sub-ground layer as if the painters had followed the formula of the tracts. Ground structure resembles that of the Indian paintings described by S. Paramasivan. As far as the other buildings examined are concerned, it seems that the technology there was different, though the binding media used in Pendjikent were similar to those of Kara-Tepe. However, all the paintings are made with paints mixed with plant gum glues.

It is of great interest that it was possible to extract polymeric polysaccharides 2000 years of age. The state of the proteins and the polysaccharides of which the binding medium consists is dependent on the conditions surrounding the paintings: the local climate, a possible influence of the fauna and the flora, etc. However, it should be remembered that a complete spontaneous disintegration of proteins takes 10^4–10^5 years [41], and that polymeric peptides and proteins have now been found in the bones and shells of animals which lived millions of years ago—among other things in dinosaur bones [42]—while polysaccharides have been found in the remnants of plants whose age amounts to 400–500 million years [43]. It is well known that, as early as the beginning of this century, it was possible to extract peptides from the tissues of Egyptian mummies, and later, in the tissues of Egyptian and Peruvian mummies, enzymes were detected which remained biologically active in spite of the thousands of years that had passed [44].

The results of our research do not contradict these data. The case of Mansur-Depe is an example of how at least a partial disintegration of proteins takes place under unfavourable conditions. A parallel with excavated bones may be drawn here: a thick $CaCO_3$ and gelatin ground resembles a wall of a hollow bone consisting of apatite and collagen. Thus, one may suppose that, even if gelatin disintegration did occur in the surface layers of the ground, it still remained intact inside. The experimental data confirm this. Free amino acids represent the disintegrated gelatin, and the amino acids revealed after the hydrolysis of the residue represent polymeric gelatin which precipitates during centrifugation of the sample solution together with pigment particles.

The same can be said about Kara-Tepe and other buildings. The conditions under which fragments of the paintings were preserved there differed from those in Mansur-Depe. Thanks to this it was almost always possible to extract polysaccharides. The binding medium in a fragment of a Kara-Tepe painting taken from a cave wall was the easiest one to extract. This is not surprising since the unfavourable influence of damaging factors was negligible here.

The experiments described make it possible to speculate about the technique of the ancient

Central Asian paintings. However, to arrive at any definite conclusions, one has to devote further study to the paintings in every room of each building already studied as well as other archaeological objects. One may hope that as a result of such work it will be possible to come to some conclusions about the similarities and differences between the artistic schools represented in the monuments of Central Asia, and to do this not only on the basis of analysing their style but also on the technology and materials used.

ACKNOWLEDGEMENT

The author is greatly indebted to Dr A. S. Antonov for his kind permission to carry out some of the experiments in the Laboratory of Bioorganic Chemistry, Moscow State University; to Drs A. Troitzky, L. Baratova and L. Belianova of the same laboratory for co-operation and for the quantitative analysis of amino acid mixtures; to Dr V. Tulchinsky of the Shemyakin Institute for Chemistry of Natural Products, USSR Academy of Sciences, for his help in interpreting the infrared spectra, and to Dr A. Usov of the Institute of Organic Chemistry, USSR Academy of Sciences, for his help with gas chromatography of carbohydrates.

REFERENCES

1 SISHKIN, V. A., *Varakhsha*, Izdatelstvo Academii Nauk SSSR, Moscow 1963, pp. 150–152.
2 DA SILVA, R. H., 'The Problem of the Binding Medium Particularly in Wall Painting', *Archaeometry*, 6 (1963), 56–64.
3 KOSHELENKO, G. A., and LELEKOV, L. A., 'Monumental Painting in Mansur-Depe', *Soobschenia VTsNILKR*, 26 (1970), 155–162.
4 STAVISKY, B. JA., in *Archaeological Discoveries 1972*, Nauka, Moscow 1973, p. 471.
5 VOROBIEVA, M. G., 'On the Technique of the Interior Decoration in the Toprak'kala Castle', *Trudy Khorezmyiskoi archeologoetnograficheskoy expedicii*, 1 (1952), 68–70.
6 BELENITZKY, A. M., *Monumental Art of Pjandzikent*, Iskusstvo, Moscow 1973, pp. 39–56.
7 LITVINSKY, B. A., and ZEIMAL, T. I., *Adzhina-Tepa*, Iskusstvo, Moscow 1971, pp. 67–76.
8 KOSTROV, I. P., 'Technique of Painting and Conservation of the Paintings of Ancient Pendjikent', in *The Paintings of Ancient Pendjikent*, Izdatelstvo Academii Nauk, Moscow 1954, pp. 162–163.
9 MOORE, S., and STEIN, W. H., 'Chromatographic Determination of Amino Acids by the Use of Automatic Recording Equipment', *Methods in Enzymology*, Vol. 6, Academic Press, New York 1969, pp. 819–831.
10 AKHREM, A. A., and KUZNETSOVA, A. M., *Thin-layer Chromatography*, Nauka, Moscow 1964, p. 9.
11 ADAMS, J. A., 'Complete Acid Hydrolysis of Polysaccharides', in *Methods of Carbohydrate Chemistry*, Mir, Moscow 1967, pp. 442–447.
12 READSWELD, C. W., and KLOMP, H., 'Thin-layer Chromatographic Analysis of Sugar Mixtures', *J. Chromatogr.*, 57 (1971), 99–106.
13 SLONEKER, J. H., 'Gas Chromatography of Alditol Acetates', in *General Carbohydrate Methods*, Academic Press, New York and London, Vol. 6, 1972, pp. 20–24.
14 KECK, S., and PETERS, T., 'Identification of Protein-containing Paint Media by Quantitative Amino Acid Analysis', *Studies in Conservation*, 14 (1969), 75–82.
15 ARMSTRONG, W. G., and TARLO, H. L. B., 'Amino Acid Components in Fossil Calcified Tissues', *Nature*, 210 (1966), 481–482.
16 HO, T.-W., 'The Isolation and Amino Acid Composition of the Bone Collagen in Pleistocene Mammals', *Comp. Biochem. Physiol.*, 18 (1966), 481–482.
17 MASSCHELEIN-KLEINER, L., and TRICOT-MARCKX, F., 'La détection de polysaccharides dans les matériaux constitutifs des œuvres d'art', *Bull. Inst. roy. Patrimoine artist.*, 8 (1965), 180–191.
18 MASSCHELEIN-KLEINER, L., HEYLEN, J., and TRICOT-MARCKX, F., 'Contribution à l'analyse des liants, adhésifs et vernis anciens', *Studies in Conservation*, 13 (1968), 105–121.

19 SCHERBUKHIN, V. D., 'The Usage of IRS for Carbohydrates' Studies', *Uspekhi biologicheskoy khimii*, Nauka, Moscow, 9 (1968), 198–219.
20 ROSIK, J., KARDOSOVÁ, A., and KUBALA, J., 'Infrared Spectra of Peach Gum Polysaccharides of Prunus persica (L) Batch, *Carbohyd. Res.*, 18 (1971), 151–156.
21 OSIPOVA, N. N., 'On the Detection of Soil Mineral Components by Infrared Spectrometry', *Biologicheskie Nauki*, No. 8 (1973), 116–120.
22 ROSIK, J., ZITKO, W., and KUBALA, J., 'Structure of Sour Cherry Tree Gum (Prunus cerasus L.)', *Collection Czechoslov. Chem Commun.*, 31 (1966), 1569–1577.
23 ZITKO, W., ROSIK, J., BRUTENIČKOVÁ, M., and KUBALA, J., 'Some Structural Features of Apricot Tree Gum (Prunus armeniaka L.)', *Collection Czechoslov. Chem. Commun.*, 30 (1965), 3501–3512.
24 COOMARASWAMY, A. K., 'The Technique and Theory of Indian Painting', *Technical Studies in the Field of Fine Arts*, 3 (1934), 59–89.
25 GUNASINGHE, S., *La technique de la peinture Indienne d'après les textes du Silpa*, Presses Universitaires de France, Paris 1957, pp. 11–16, 53–54.
26 PAINTER, 'Techniques anciennes de la peinture Hindoue', *Peintures, Pigments, Vernis*, 42 (1966), 633–637.
27 AGRAWAL, O. P., 'A Study of the Techniques of Indian Wall Painting', *J. Indian Museums*, 25–26 (1969–70), 99–119.
28 BUSSAGLI, M., 'Ajanta', in *Encyclopedia of World Art*, McGraw Hill Book Co. Inc., New York, Vol. I (1959), pp. 159–178.
29 PARAMASIVAN, S., 'Technique of the Painting Process in the Brihadesvara Temple at Tanjore', *Nature*, 137 (1936), 867–868.
30 PARAMASIVAN, S., 'Technique of the Painting Process in the Cave Temple at Sittannavasal', *Nature*, 139 (1937), 114.
31 PARAMASIVAN, S., 'Technique of the Painting Process in the Temple of Vijayalaya Chilisvaram in the Pudukkottai State', *Proc. Ind. Acad. Sci.*, 7 (1938), 282–293.
32 PARAMASIVAN, S., 'The Pallava Paintings at Conjeevaram—an Investigation into the Methods', *Proc. Ind. Acad. Sci.*, A. 10 (1939), 77–84.
33 PARAMASIVAN, S., 'The Wall Paintings in the Bagh Caves—an Investigation into their Methods', *Proc. Ind. Acad. Sci.*, A. 10 (1939), 85–95.
34 PARAMASIVAN, S., 'An Investigation into the Methods of the Mural Paintings, A: In Cochin and Travancore. B: Lepakshi and Sanpalayam', *J. Ind. Soc. of Oriental Art*, 7 (1949), 18–38.
35 DUDIN, S. M., 'Technique of Wall Painting and Sculpture in Ancient Buddhist Caves and Temples in Eastern China', *Sbornik muzeya archeologii i etnografii, Petrograd*, 5 (1917), 21–92.
36 GETTENS, R. J., 'The Materials in the Wall Paintings of Bamyan, Afghanistan', *Technical Studies in the Field of Fine Arts*, 6 (1937–38), 186–193.
37 GETTENS, R. J., 'The Materials in the Wall Paintings of Kizil in Chinese Turkestan', *Technical Studies in the Field of Fine Arts*, 6 (1937–38), 132–138.
38 ZAKHIDOV, P., *Fergana wall painting*, Gosudarstvennoe izdatelstvo Khudojestvennoi literatury UzSSR, Tashkent 1960, p. 10.
39 SCHERBUKHINA, N. K., 'Reserve Glucomannannes of Higher Plants', *Uspekhi biologichskoy khimii*, 9 (1970), 226–243.
40 ANDREEV, N. N., 'A Biological Method Used for Detection of Binding Medium in Paintings', *Muzeinoe delo*, 6 (1927), 5.
41 ABELSON, P., 'Geochemistry of Amino Acids', *Intern. Ser. Monogr. Earth Sci.*, 16 (1963), 431–453.
42 MILLER, M. F., and WYCKOFF, R. W. G., 'Proteins in Dinosaur Bones', *Proc. Nat. Acad. Sci.*, 60 (1968), 176–178.
43 SWAIN, F. M., *Fossil Carbohydrates, in Organic Geochemistry*, Springer-Verlag, Berlin-Heidelberg-New York 1969, pp. 374–400.
44 JONES, J. D., and VALLENTYNE, J. R., 'Biogeochemistry of Organic Matter. I. Polypeptides and Amino Acids in Fossils and Sediment in Relation to Geochemistry', *Geochim. Cosmochim. Acta*, 21 (1960), 1–34.

Received 17 June 1974

VADIM J. BIRSTEIN, born 1944, graduated from the Department of Plant Biochemistry, Moscow State University, in 1966. He was a postgraduate in the Kurchatov Institute of Atomic Energy and then, in 1971, joined the staff of VTsNILKR laboratory. In 1972 he obtained the degree of Candidate of Biological Sciences.

Author's address: All Union Central Scientific Research Laboratory for Conservation and Restoration, VTsNILKR, Krestyanskaya pl, 10, Moscow J-172, USSR.

Abstrait—Ont été l'objet d'études les composantes organiques de couches picturales et des enduits dans des exemples de peintures murales de l'Asie Centrale, datant de la dernière période de l'Antiquité et du début du Moyen-Age. Des analyses quantitatives d'acides aminés, séparés d'echantillons des peintures murales de Mansur-Depe (2me au 1er siècle av. J.C.) ont démontré qu'il a été fait usage de gélatine pour la préparation de liants de peinture et des enduits (un pourcentage élevé de proline, de glycine et d'alanine a été découvert sans trouver de traces d'hydroxyproline). Dans d'autres peintures murales des 2me et 8me siècles, l'utilisation de gommes végétales a été supposée, étant donné que des polysaccharides, séparés des echantillons, montraient un spectre infrarouge, ressemblant à ceux des polysaccharides de la sous-famille des *Prunoideae*. La gomme utilisée dans les peintures murales de Toprak-Kala (3me et 4me siècles) et dans une peinture de Khiva du dix-neuvième siècle a pu être identifiée de façon précise; il s'agit soit de gomme d'abricotier soit de gomme de cérisier. La technique pratiquée pour la préparation de peintures et des enduits à Mansur-Depe et à Kara-Tepe (2me et 4me siècles) ressemble à celles qui ont été décrites dans des manuscrits indiens du Moyen-Age.

Kurzfassung—Organische Komponenten von Farbschichten und Putzen in Proben spätantiker und frühmittelalterlicher Wandgemälde aus Zentralasien wurden untersucht. Eine quantitative Analyse von Aminosäuren, die aus Proben von Mansur-Depe Wandgemälden (2. bis 1. Jahrhundert v. Chr.) isoliert worden waren, hat gezeigt, dass für die Herstellung von Farbmitteln und Putzen Gelatine angewandt wurde (Proline, Glycine und Alanine waren mit einem hohen Prozentsatz vertreten, während Hydroxyproline nicht entdeckt wurde). In anderen Wandgemälden des 2. bis zum 8. Jahrhundert konnte der Gebrauch von Pflanzengummiarten gefolgert werden, da die aus den Proben isolierten Polysacchariden infrarote Spektra aufwiesen, die denen der Polysacchariden der *Prunoideae* Subfamilie entsprechen. Das in Toprak-Kala Wandgemälden (3. bis 4. Jahrhundert) und in einem Gemälde von Khiva aus dem neunzehnten Jahrhundert angewandte Gummi konnte genau ermittelt werden: es war entweder Aprikosen-oder Kirschgummi. Die bei der Herstellung von Farbstoffen und Putzen in Mansur-Depe und Kara-Tepe (2. bis 4. Jahrhundert) angewandte Technik entspricht der in mittelalterlichen indischen Manuskripten beschriebenen Technik.

Riassunto—Si esaminavano componenti organici di strati di pittura e intonaci in campioni di pitture murali centro-asiatiche della tarda antichità e del primo medioevo. L'analisi quantitativi di aminoacidi isolati da campioni di pitture murali di Mansur-Depe, II-I secolo a.C., ha dimostrato che si usava la gelatina per la preparazione dei strati di pittura e del intonaco (un'alta percentuale di prolina, di glicina e di alanina è stata trovata, mentre non fu scoperta la idrossiprolina). In altre pitture murali dei secoli II-VIII, l'uso di gomme vegetali è da supporre, dato che i polisaccaridi isolati dai campioni mostravano spettri infrarossi assomiglianti a quelli dei polisaccaridi della sottofamiglia delle *Prunoideae*. La gomma adoperata in pitture murali di Toprak-Kala, sec. III-IV, ed in una pittura ottocentesca di Khiva, si è potuta identificare con esattezza: era gomma di albicocco o di ciliegio. La tecnica applicata per la preparazione di colori e intonaci a Mansur-Depe ed a Kara-Tepe, sec. II-IV, assomiglia a quelle descritte in manoscritti indiani medievali.

Extracto—Se examinaron los componentes orgánicos de capas de pintura y de fondos en especímenes de pinturas murales de Asia Central del último período de la Antigüedad y el primer período de la Edad Media. El análisis cuantitativo de amino ácidos, aislados de especímenes de pinturas murales de Mansur-Depe, siglo II-siglo I a. de J.C., demonstró que se empleó gelatina para la preparación de medios de pintura y de fondos (prolina, glicina y alanina se relevaron en un porcentaje elevado y no se descubrió hidroxiprolina). En otras pinturas murales, del siglo II hasta el siglo VIII, se dedució el uso de gomas de plantas, puesto que las polisacaridas, aisladas de los especímenes, mostraron espectros infra-rojos parecidos a los de las polisacaridas de la subfamilia de *Prunoideae*. Se pudo identificar con precisión la goma empleada en pinturas murales de Toprak-Kala, siglo III-siglo IV y también en una pintura del siglo XIX de Khiva: fue goma de albaricoquero o bien de cerezo. La técnica usada para la preparación de pinturas y de fondos en Mansur-Depe y en Kara-Tepe, siglo II-siglo IV, se parece a las técnicas descritas en manuscritos indios medievales.