Original Paper

Micro Analysis on Hallstatt Textiles: Colour and Condition

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Abstract. Due to the special conditions in the Bronze Age and Hallstatt Period salt-mines of Hallstatt, Austria, a large number of archaeological textile fragments, dated from 1400 to 400 BC, can be found. Textiles of good condition from these periods are quite unique. The fibres are identified as wool and most of the fragments still have colours i.e. yellow, green, olive-green, brown, blue and black. To obtain information about the dyeing techniques used in this period, dyestuff analyses are performed by high performance liquid chromatography coupled to photo diode array detection (HPLC-PDA) and mordant analysis by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS). In addition, the condition of the textile fibres is assessed by SEM. The analyses revealed that all textiles were dyed with plant dyes and insect dyes. The yellow plant dyes and the red insect dyes are mordant dyes but the identification of mordants turned out to be difficult. SEM/EDS analyses of small uncontaminated areas on the fibre showed that the elements aluminium, iron and copper are present in many samples. These elements could originate from a mordant or from the mine. The condition of the fibres was assessed by the presence of the characteristic scales on the wool, tears, cuts and particles from the mine. It was found that a relation exists between the copper content of the fibres and their condition.

Degraded fibres contain more copper. Black textile fragments which are most possibly coloured by iron gall-black show as well degradation phenomena.

Key words: Hallstatt textiles; SEM; dyestuff analysis; element analysis; condition of the fibres.

Due to the special conditions of the prehistoric salt-mine of Hallstatt, Austria, a large number of archaeological textile fragments, dated from 1400 to 400 BC, are found. These textiles including their colour are in a relatively good shape due to the impregnation by salt, the constant climate of the mine and the fact that the textiles were protected from light for more than 2000 years. Prehistoric textiles of good condition from the Bronze Age (after 1400 BC) and the Hallstatt Period (800–400 BC) are quite unique. The fibres are identified as wool and most of the fragments still have colours, i.e. yellow, green, olive-green, brown, blue and black. The fragments were found embedded in the “heathen’s rock” (Heidegenbiegel), a layer containing salt, clay, gypsum, broken shafts, countless spills of spruce and fir used as torches, food remains and parts of broken bronze tools [1].

In 2002 a multidisciplinary research project, Halltex I, started with the investigation of the coloured textiles from the prehistoric mines of Hallstatt. The pilot project was a collaboration between the Netherlands Institute of Cultural Heritage (ICN) in Amsterdam, the Prehistoric Department of the Natural History Museum

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Vienna (NHM) and the Department Archaeometry of the University of Applied Arts Vienna. The aim of the project was to investigate if the woollen textile fragments were dyed and if so, which dyes and dyeing techniques were used.

This study focuses on the condition of the fibres and the presence of chemical elements affecting the colour of the fibres. It was of interest to study whether the elements were used as mordants or came into fibres while textiles lay embedded in the “heathen’s rock”.

Mordant Dyeing

 Principally three different sorts of organic colorants, dyestuffs, tannins and the organic pigment indigotin, and three different dyeing techniques, mordant dying, direct dyeing and vat dying, could have been used in prehistoric times. Most of the water-soluble red and yellow dyestuffs are mordant dyestuffs, which could also be called metal complex dyestuffs. Co-ordination metals of metal salts, e.g. from mordants containing aluminium, iron or copper, are able to form a chemical bond between dyestuffs and fibres producing a stable dyeing on a textile. In prehistoric times different sources of metal salts were available. It is not known if alum, $\text{Al}_2(\text{SO}_4)_3\cdot\text{K}_2\text{SO}_4\cdot24\text{H}_2\text{O}$, or other inorganic aluminium sources were at hand for dyeing in prehistoric Europe. Beside natural copper and iron salts by the use of natural acidic substances such as vinegar one could have produced corrosion products (metal salts) on bronze, copper and iron objects and applied them as mordant. Iron containing mud and aluminium accumulating plants of the clubmoss family could have been used as well.

Materials and Methods

Samples were taken from each of the characteristic shades found on the textiles of Hallstatt, altogether 17 samples from 16 textile fragments (Fig. 1). In addition, reference samples which were dyed using ancient recipes for dyeing were analysed by SEM/EDS to test the detection level of the chemical elements present in the mordant.

Prior to dyestuff analysis, all samples were investigated under an optical light microscope (OLM) by incident and transmitted light (magnification 20–600x). These techniques were used to identify the fibres, to observe the condition of the fibres and the regularity of the colour within the yarns and the fibres.

The samples were analysed by scanning electron microscopy (SEM, JEOL JSM5910LV) equipped with an energy dispersive X-ray spectrometer (EDS, Vantage from ThermoNoran). SEM was used to study the deterioration and contamination of the textile fibres and EDS for elemental analysis of the fibres to study the presence of mordants and to investigate if the samples were contaminated with elements originating from the mine. To avoid surface charging the material was coated with carbon. The SEM was operated at an accelerating voltage of 15 and 20 keV, high-performance liquid chromatography coupled to photo diode array detection (HPLC-PDA) was used to obtain information about the dyestuffs. The results of the dyestuff analysis are published in Hoffmann-de Keijzer et al. (2005) [2].

Results and Discussion

Fibre Analysis

SEM analysis of the fibres showed that in most of the samples the scales typical for wool were degraded (Fig. 2). In addition, the surface of nearly all the samples was contaminated with inorganic particles. Some samples were even heavily soiled (Fig. 3). The samples with the scales completely disappeared, also showed tearing and cracking of the fibres (Fig. 4). The degradation of the fibres could have taken place at different times, during the wearing of the textiles and their secondary use in the mine, during the time they were deposited in the mine and after they were excavated. An attempt was made to relate the damage of the fibres to wear and/or to degradation due to burial [3, 4].

One textile sample shows a brush-like fracture, which is characteristic for wear resulting in fatigue damage (Fig. 5). The fibres break down into their structural units, macrofibrils or fibrils. This occurs after extensive flexing and is caused by heavy strain (stress) of the fibre presumably during wear or the secondary use of the textile in the prehistoric mine. The degradation of the scales seems to be related to the concentration
of copper and the combination of iron and tannins (Table 1). The mechanism of degradation caused by the combination of a tanning substance and an iron compound has been studied extensively in the case of iron-gall ink corrosion on paper [5]. The degradation is caused by hydrolysis due to acidic components and by oxidation catalysed by free Fe$^{2+}$ ions. However, there are important differences between the use of iron-gall ink on paper and on textiles [6]. For instance, after the dyeing process the textile is rinsed thoroughly removing the acid. Therefore, the degradation of black textiles is caused mainly by oxidation, initiated by the remains of the Fe$^{2+}$ compounds. Unfortunately, the presence of free Fe$^{2+}$ ions on the fibres has not been tested but the presence of transition metal copper is also known to initiate oxidative degradation of organic material [7]. The process of ageing due to oxidation, hydrolysis and light can lead to the formation of brit-
tle breaks (Fig. 6 [4]). The degradation of the scales and the tearing of the fibres could have been the result of the use of iron-gall black to dye the textile combined with the copper-rich burial conditions in the mine. It is not possible to establish whether the tears and cracks in the fibres were formed during burial in the mine or after excavation.

Element Analysis

HPLC analyses revealed that all textiles were dyed with plant dyes and insect dyes (Table 1). The yellow plant dyes and red insect dyes are mordant dyes but the identification of the mordants turned out to be difficult. Figure 6 shows that it is possible to detect the chemical elements aluminium and iron on a small area, about 30 × 30 μm, of a single textile fibre of dyed reference material by EDS. However, the peaks are rather small indicating that the amount of metal salts is around the detection limit of the EDS detector [8]. It was necessary to analyse such a small area since it was observed by OLM and SEM that many fibres of the Hallstatt textiles are contaminated with different sorts of particles. Therefore, small areas of a single fibre, free of particles, were analysed. For comparison, the particles themselves were analysed separately.

Using SEM/EDS several elements were detected (Table 1). Three elements, i.e. carbon, oxygen and sulphur were detected in large quantities. They are part of the wool protein. In many samples of the Hallstatt textiles the presence of aluminium, iron and copper was shown by EDS analyses of uncontaminated areas on the fibre (Fig. 7). The particles consist of aluminium silicates and salts (Fig. 8). Aluminium, iron and copper could not only originate from a mordant but also from the mine since the textile fragments could have

![Image](image.png)

**Fig. 5.** Hallstatt textiles, fibre analysis, degradation of wool fibres monitored with SEM. SE image of a fibre with a brush-like fracture indicating heavy stress presumably during wear or secondary use of the textile in the mine, brown sample 78851 © ICN Amsterdam

<table>
<thead>
<tr>
<th>Colour</th>
<th>Dyestuff</th>
<th>Source</th>
<th>Fe</th>
<th>Cu</th>
<th>Al</th>
<th>Si</th>
<th>Mordant</th>
<th>Scales*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>Indigotin, Indirubin, Isatin</td>
<td>woad</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td>-/0</td>
</tr>
<tr>
<td></td>
<td>Quercetin, Probably carminic acid</td>
<td>unknown yellow dye</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kermesic acid</td>
<td>insect dye</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Ellagic acid</td>
<td>tannin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ellagic acid equivalent</td>
<td>probably orchil</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Indigotin</td>
<td>woad</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Black</td>
<td>Yellow or red dyestuffs</td>
<td>likely weld</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>oo</td>
</tr>
<tr>
<td></td>
<td>Luteolin, Apigenin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown</td>
<td>Luteolin, Apigenin</td>
<td>likely weld</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>Iron*</td>
<td>-/oo</td>
</tr>
<tr>
<td></td>
<td>Apigenin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Copper*</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>Indigotin, Probably orcein</td>
<td>woad</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Copper*</td>
<td>o</td>
</tr>
<tr>
<td></td>
<td>Luteolin</td>
<td>probably orchil</td>
<td></td>
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<td></td>
<td>Copper*</td>
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</tr>
<tr>
<td></td>
<td>Apigenin</td>
<td>wold</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Olive-green</td>
<td>Luteolin, Apigenin</td>
<td>likely weld</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>Copper*</td>
<td>-</td>
</tr>
</tbody>
</table>
been embedded in a layer with aluminium or iron-containing minerals or in a layer containing pieces of bronze tools. Corrosion products of copper from these tools have been found to cover some textile fragments. As mordant dyes were identified the use of mordants can be assumed, because mordants are necessary to obtain fast colours. Yet it was not possible to differentiate between a deliberate mordant dyeing process and a “post mordanting effect” caused by a solution containing aluminium, copper and iron salts in the mine. While aluminium salts do not change the colours of dyed textiles severely iron and copper salts cause darkening of yellow and red mordant dyes and tannin dyes and the colouration of the wool fibre when no dyes are present.

Olive-green and olive-brown shades are obtained when yellow flavonoid dyes (quercetin, luteolin, apigenin) are mordanted with iron or copper ions; dark red and violet shades yield by red anthraquinone dyes (carmine acid, kermesic acid) and iron or copper mordants. Browns dyed with tannins turn into black when they are treated with iron salts (iron-gall black) while copper salts do not influence tannin browns. Iron and copper ions seem to have affected the final colour of the textile fragments either originating from mordants or from the mine. When these metal salts penetrated into the textiles during their deposition in the mine they caused changing of the original colour. The blue colour in Hallstatt textiles was obtained by using woad in combination with insect dyes, yellow dyes and tannins. The yellow colour was dyed using a mordant dye, likely weld.
**Conclusions**

The condition of the fibres is a combination of wear during prehistoric time, the secondary use in the prehistoric mine and the degradation by ageing during burial in the mine and after excavation. The degradation of the scales and the tearing of the fibres seem to be related to the concentration of copper and the combination of iron and tannins.

The textiles were coloured using complicated dyeing techniques such as vat dyeing with woad and mordant dyeing with yellow and red dyes. Due to severe contamination of the fibres it was not possible to identify the mordants used with certainty. However, the black textiles are most probably dyed with iron-gall black and the additionally use of woad, red and yellow dyestuffs. In case of the brown, reddish-brown, green and olive-green textiles it was not possible to determine whether the elements copper and iron, affecting the final colour of the textile fragment, originate from a mordant or from the mine.

**Acknowledgements**. We would like to thank all persons and institutes who helped us realize this project, especially Dr. Anton Kern and Dr. Fritz Eckart Barth from the Natural History Museum Vienna.

**References**


HPLC analysis of the black textiles revealed that woad and tannins were used and most probably also weld and unknown red dyestuffs. Both of the samples contain iron whereas no copper was detected. Although theoretically, the iron could originate from the salt mine, it is likely that an iron-bearing mordant was used together with tannins to get an iron-gall black.

In case of the green and olive-green textile fragments it remains uncertain whether a mordant was used or not. HPLC analysis indicated that for the green colour the vat dye woad and a yellow mordant dye (likely weld) and copper-ions were used. Yet the use of copper as a mordant could not be confirmed. Most of the copper found in the green and olive-green fibres seems to be a contamination from the mine since also silica has been identified and in the case of the green samples, iron and silica.

HPLC analysis of the brown and reddish-brown textiles revealed the use of woad, likely weld, and probably orchil. It was impossible to determine whether the elements found in the fibres could have been applied as a mordant or were contaminants from the mine. However, the colour observed can be the effect of the presence of iron and copper.

Conclusions

The condition of the fibres is a combination of wear during prehistoric time, the secondary use in the prehistoric mine and the degradation by ageing during burial in the mine and after excavation. The degradation of the scales and the tearing of the fibres seem to be related to the concentration of copper and the combination of iron and tannins.

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