Methods of Chemical and Physicochemical Analysis in the Identification of Archaeological and Historical Textiles

Abstract
The main problem hindering proper analysis and documentation of archaeological and historical textiles is the lack of co-operation between scientists dealing with different aspects of these objects – archaeological, artistic, historical and technological. The last one includes the examining of manufacturing methods and analysis of the raw material and dyes used by chemical and physicochemical analysis methods, which is fundamental for proper identification of the object, as well as its origin and dating. The methods include: SEM, ICP, ATR/FTIR and AAS for determination of the raw material and other components of the object, the archaeological environment, analysis of the biodeterioration of archaeological textiles, as well as HPLC for analysis of the colour. This paper presents the methods and exemplary results of research conducted by the authors at the Technical University of Lodz, involving the analysing of archaeological textiles from the area of Poland and historical textiles from the collections of Polish museums.

Keywords: archaeology, historical textiles, chemical analysis, physico-chemical analysis, SEM, ICP, ATR/FTIR, AAS, HPLC.

Introduction
When compared with archaeological and museal objects of more a durable nature, such as ceramic or metal ones, textiles are very fragile, and in danger of deterioration every time they are analysed. Growing awareness of their value for many different areas of science has resulted in increasing interest and numerous publications; however, there still exist old collections of archaeological and historical textiles only cursorily analysed. New standards of documentation with use of modern non-destructive analytical methods are necessary if we want to preserve them for the next generations. Proper documentation of these objects requires cooperation between researchers representing different areas of science, like archaeology, chemistry, textile technology, and the history of art [1].

There are several factors that make the analysis of archaeological and historical textiles especially difficult. One obvious factor is fibre degradation. It can result in a change of physical, chemical and structural properties, such as a decrease in the thread and fabric strength, or even in distortion of the whole object. Analysis requires the application of special, less destructive testing methods, which, at the same time, are sensitive enough to determine the parameters or properties changed due to object ageing.

From the point of view of identification of textiles, the most important properties can be divided into three groups: the nature of fibres, the colour and structure of threads and fabric. The fabric structure includes the properties of threads used, the weave pattern, the number of wefts and warps per centimetre and the yarn crimp. The nature of fibres not only means the kind and origin (wool, silk, flax, etc), but also the fibre diameter and length. The colour means the kind of dye.

Research undertaken by a research group from the Technical University of Lodz in co-operation with the Institute of Archaeology and Ethnology, the Polish Academy of Science and the National Museum in Warsaw allowed to establish new standards of analysis and documentation of historical and archaeological textiles. They include some modern methods of chemical and physicochemical analysis.

The aim of the paper is to present the methods applied and some exemplary results obtained by the group from its work on archaeological textiles from the area of Poland and historical textiles from the collection of the Lowicz Cathedral.
collections of Polish museums. This paper presents the application of methods in three main areas – analysis of the raw material, identification of dyes and analysis of the biodeterioration of archaeological textiles. The methods include SEM (scanning electron microscopy), ICP (inductively coupled plasma mass spectrometry), ATR/FTIR (attenuated total reflection using infrared Fourier transform spectroscopy), and AAS (atomic absorption spectroscopy) for determination of the raw material, some other components of the object, the archaeological environment and HPLC (high performance liquid chromatography) – for analysis of the colour.

Biodegradation of textiles

Microbiological deterioration is one of the most important factors determining the durability of textile materials, which can be chemically assimilated (treated as a nutrient for microorganisms) or dissimilated (destroyed by metabolites produced by them). Most archaeological textiles stay in the soil, where a variety of microorganisms can be found, such as bacteria, actinomycetes, fungi, algae and protozoa. Microbes emit acid radicals causing chemical processes typical for corrosion. Very important factors are the properties of the environment in which decay takes place – humidity, pH, light, temperature, ventilation and material properties – the chemical constitution, structure and other compounds of the object, such as mordants, dyes, adhesives and finishes, which can slow down or accelerate the biodeterioration processes.

Natural fibres are especially susceptible to bio-corrosion due to the content of chemical individuals being a nutrient for microorganisms, among which the most dangerous for textiles are fungi: Alternaria, Aspergillus, Fusarium, Mennoniella, Myrothecium, Neurospora, Penicillium, Scopulariopsis, Stachybotrys, Stemphylium and bacteria: Cellvibrio, Cellulaccola, Microspora, Clostridium. Celulose fibres include cotton, flax, hemp and other vegetable fibres. Cellulose is decomposed in enzymatic hydrolysis by both fungi (Chaetomium, Myrothecium verrucaria, Mennoniella echinata, Stachybotrys atra, Trichoderma, Penicillum, Aspergillus and bacteria Cytophaga, Cellulomonas, Cellulibrio, Bacillus and Clostridium). Susceptibility to decay depends on the contribution of fibre compounds: cellulose, lignin, and non-cellulosic compounds such as pectines, hemicellulose and proteins [2].

Wool fibre consists of three types of proteins called keratins, with chemical bonds that can be decomposed by enzymes (proteases) causing keratinase. Wool can be destroyed mainly by fungi: Trichophyton, Myrothecium, Aspergillus, Penicillium, Chrysosporium, Ctenomyces, bacterium: Bacillus (Bacillus subtilis, Bacillus cereus, and Bacillus mycoides), Cytophaga, Pseudomonas aeruginosa Proteus vulgaris, Actinomycetes, Alcaligenes brookeri; actinomycetes: Streptomycetes fradiae and others. The decay process, humidity and the presence of microbes also result in the yellowing

Figure 2. 12th century stole from Kruszewica with well preserved fabric under the metal thread embroidery [5].

Figure 3. Fragments of archaeological textiles. From the left: 17th silk fabric from Kostrzyn, Roman period wool fabric – Nowy Lowicz, medieval wool fabric – Elblag.
of wool. The basic factor determining the durability of wool is its alkalinity (pH: 8.0-8.5).

Raw silk consists of protein fibres called fibroins combined with sericin, which is responsible for the silk yellowing but, at the same time, increasing the durability of silk. Among the microorganisms causing silk decay are the following bacteria: Bacillus megaterium, Pseudomonas cepacia, Serratia, Streptomyces, Variovorax paradoxus, and the fungus Aspergillus niger. The process of biodegradation can be accelerated by light, which is very important for historical textiles often exposed to it in museums [3].

In the case of historical fabrics, one of the most hazardous factors is UV radiation, resulting in a loss of fibre strength and the photochemical degradation of dyes, which results in a change of colour [4]. Historical textile objects usually have the left side better preserved due to less exposure to light, but also because of the lining. Thus to determine the original colour, the fragments which had not been exposed to light before used, like these under the lining, seams or fastening slats (Figure 1, see page 67).

The last cause of damage we would like to mention, especially in historical textiles, are insects. This mainly concerns textiles made from fibres containing keratin, like wool.

Despite the fragility of textiles, well preserved objects can often be found. Except for climate, the most important factor affecting textile durability is contact with metal objects, for example, fabrics made with the use of metal threads (Figure 2) [5]. Textiles also survive when in contact with jewellery, pots, spurs, or in metal coffins [6].

ICP–AES (inductively coupled plasma – atomic emission spectroscopy)

ICP can be very helpful in the analysis of the biodeterioration of textiles. It allows the identification of the atoms of metals which were an integral part of the fabric as decorative elements – metal threads, sequins, or in chemical compounds used as dyes. The presence of some metals can slow the decay process down due to their antibacterial features. In this way the method can help in the analysis of some factors influencing the durability of textiles.

A sample in the form of a demineralised solution is put in a stream of ionised argon plasma of temperature 6000-10000 K. Inducted in this way, the elements emit a characteristic spectrum of the range given in Table 1. Using this method, one can determine dozens of elements of concentration 0.1-10 ppb (µg/dm³).

This method was used for analysis of the fragments of archaeological textiles presented in Figure 3. The aim was to determine the content of metal contaminants in the samples. Results of the analysis are presented in Table 1.

The content of specific metals in the samples is different. However, the content of copper and silver in samples 1 and 2 is considerably higher. The same concerns the content of lead in the latter sample. All these metals are known for their bac-

<table>
<thead>
<tr>
<th>Metals</th>
<th>Absorption (max), nm</th>
<th>Detection limit, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (silver)</td>
<td>328.07</td>
<td>6</td>
</tr>
<tr>
<td>Cu (cuprum)</td>
<td>324.75</td>
<td>2</td>
</tr>
<tr>
<td>Mn (manganese)</td>
<td>257.51</td>
<td>1</td>
</tr>
<tr>
<td>Mg(magnesium)</td>
<td>279.08</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn (zinc)</td>
<td>231.86</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1. Range of UV radiation spectrum for exemplary elements.

<table>
<thead>
<tr>
<th>Metal sample</th>
<th>A1, mg/kg</th>
<th>A2, mg/kg</th>
<th>A3, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>171.82</td>
<td>140.47</td>
<td>56.22</td>
</tr>
<tr>
<td>Pb</td>
<td>10.68</td>
<td>18.33</td>
<td>83.37</td>
</tr>
<tr>
<td>Cu</td>
<td>412.73</td>
<td>6738.74</td>
<td>42.58</td>
</tr>
<tr>
<td>Ag</td>
<td>1115.91</td>
<td>514.92</td>
<td>4.42</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.004</td>
<td>&lt;0.004</td>
<td>&lt;0.004</td>
</tr>
</tbody>
</table>

Table 2. Content of metals in analysed samples of archaeological textiles.
tericidal and bacteriostatic properties, and their high concentration can result in higher durability of textiles.

Another method that was recently used for a similar purpose is the Laser Ablation Inductively Coupled Plasma Time of Flight Mass Spectroscopy (LA-ICP-TOF-MS) [7]. It was applied to test the Wawel arrases in order to determine the content of metals in tapestry samples. The main advantage of the method is that the samples analysed do not need any preparation. However, with no standards available, it was only possible to determine the relative intensity of metal ions. For this reason the results obtained can not be used for comprehensive analysis.

Simple physical tests such as burning quickly identify animal fibres, which do not burn readily nor shrivel into a residue of carbon. These fibres usually emit the distinct odour of singed hair. Vegetal fibres burn easily to a fine ash. Many fi-

Figure 6. FTIR/ATR analysis – the spectra of three samples of wool – standard, medieval and from the 2nd century.

Figure 7. FTIR/ATR analysis – the spectra of three samples of silk – standard, medieval and from the 18th century.

Figure 8. Fragments of chasuble found during the restoration of the Colegiate Church in Tum, Poland.

Figure 9. Wool fabric from the 2nd century from Gronowo and its reconstructed.

Identification of the raw material
bres and hairs can be readily identified by microscopic examination. For instance many animal hairs can be identified by their characteristic cuticle patterns and medullar cross-sections.

**Scanning electron microscopy (SEM)**

To identify raw materials, there are more sophisticated methods. One is SEM by which we can analyse the morphology of fibre and fabric surfaces.

SEM was applied in the analysis of archaeological textile samples of finds from the Roman period and the Middle Ages. Tests were performed using a JSM-5200LV JEOL scanning electron microscope with the use of a semiconductor detector of backscattered electrons, enabling observation of the sample without initial preparation (the samples were not coated with gold). The method applied is not destructive, enabling the re-testing of the same sample with another method. Moreover, the use of the BEI-COMPO detector makes it possible to differentiate with respect to the brightness contrast, and substances of different chemical structure covering the samples, resulting from pollution or the finishing process of the textiles. The brightness contrast noticed in the image of an object of complex chemical structure depends also on the chemical constitution of the object – the higher the atomic number of the elements, the higher the emission of backscattered electrons is. Observations of fibres and other examined objects were carried out using an accelerating voltage of 25 kV in a low vacuum (LV – air pressure in the specimen chamber of the microscope 1-100 Pa), with a magnification from 50x to 2000x. The images were registered with a SEMAFORE digital system.

This method was used to identify the raw material of the decorative braided string shown in Figure 4a. The string was found at the Wielbark graveyard, originating from the late Roman period (3rd century). Using an optical microscope, the fibres were difficult to identify due to their very small diameter, and from the first sight they looked like silk. However, SEM analysis allowed to identify the material as flax, due to “nodes” typical for linen, which can clearly be seen. In Figure 4b one can see the SEM image of medieval tablet-woven silk fabric. Comparison of the two types of fibre allows to state that the linen fibre is as fine as the silk one. It proves the high quality of linen clothes from the Roman period.

The next two figures present wool fibres from clothes of the Roman (Figure 5a) and medieval periods (Figure 5b). Comprehensive analysis shows that medieval wool (15th century) was much thicker than that from the 2nd century. It confirms the premise that there was a very high level of wool manufacturing in the Roman period [8].

**Infrared spectroscopy**

Another method used for identification of the raw material is FTIR spectroscopy. It allows identification of the chemical structure of the material from which the sample was made. Comparison between the IR absorption spectrum of the archaeological fabrics analysed and reference fabrics allows to identify the nature of fibres, even if the fabric is carbonated [9].

In the analysis of archaeological textiles by means of IR spectroscopy, an ATR attachment from the company PIKE was used. The basic element of ATR is a diamond prism of size 2x2 mm, which determines the minimum size of the sample. Based on the total reflection method, ATR allows to analyse the surface of the sample totally non-invasively to a depth of 0.25 micrometres. The IR spectrum (range 7800-500 cm⁻¹) allows the identification of organic compounds in the outer layer of the sample. Some problems in the measurement can be caused by dust, different types of dirt, mordants, decay products and metal particles accumulated on the surface of fibres.

Figure 6 shows the spectra for three samples of wool fabric – standard, and two archeological: medieval and from the 2nd century. Despite the peaks related to some other compounds of the sample mentioned above, the spectra show some characteristic features allowing to undoubtedly identify the raw material. The same concerns the spectra obtained for the three silks presented in Figure 7 – standard, medieval archaeological silk and 18th century historical silk. Although both wool and silk are protein fibres, the distinctions in the spectra characteristics are significant. It proves that ATR/FTIR can be successfully applied in the identification of raw material. The small size of the samples, the very quick analysis and non-destructive character are the main advantages of the method.

In future investigations we intend to use a FTIR spectrometer coupled with a microscopic hors-d’oeuvre. It will permit to preliminary study the surface of a sample and then to indicate the points of special interest in which some features or particles are noticed, as well as to perform measurements in a precisely chosen place on the surface of the object. It should allow to apply ATR/FTIR for the identification of finishing materials such as dyes, or other specific compounds of the sample.

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**Table 3. Exemplary vegetable used for colouring textiles and chemical compounds [13].**

<table>
<thead>
<tr>
<th>Vegetable</th>
<th>Dyes</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaccinium myrtillus</td>
<td>gallic acid, ellagic acid</td>
<td>yellow</td>
</tr>
<tr>
<td>Rubia tinctorium</td>
<td>alizarin, purpurin</td>
<td>red</td>
</tr>
<tr>
<td>Salix</td>
<td>gallic acid ellagic acid</td>
<td>yellow</td>
</tr>
<tr>
<td>Sorbus aucuparia</td>
<td>gallic acid</td>
<td>brown</td>
</tr>
<tr>
<td>Acrotostaphy/os urae ursi</td>
<td>gallic acid, ellagic acid</td>
<td>yellow</td>
</tr>
<tr>
<td>Alchemilla herba</td>
<td>ellagic acid quercetin campherol luteolinramnetyna</td>
<td>yellow</td>
</tr>
<tr>
<td>Bereroeris vulgaris</td>
<td>berberin, quercetin</td>
<td>yellow-brown</td>
</tr>
<tr>
<td>Betula alba</td>
<td>myricetin, quercetin campherol, luteolin</td>
<td>yellow-brown</td>
</tr>
<tr>
<td>Equiseti</td>
<td>ellagic acid, luteolin, campherol</td>
<td>yellow</td>
</tr>
<tr>
<td>Galium vennum</td>
<td>purpurin</td>
<td>red</td>
</tr>
<tr>
<td>Galia turbica</td>
<td>gallic acid, ellagic acid</td>
<td>brown</td>
</tr>
<tr>
<td>Hyperici herba</td>
<td>quercetin</td>
<td>green-yellow</td>
</tr>
<tr>
<td>Lawsonia internis</td>
<td>gallic acid, lawson</td>
<td>yellow</td>
</tr>
<tr>
<td>Polygonum avicula/are</td>
<td>luteolin campherol</td>
<td>green-yellow</td>
</tr>
<tr>
<td>Quercus robur</td>
<td>gallic acid, ellagic acid, campherol, quercetin</td>
<td>brown</td>
</tr>
<tr>
<td>Rezeda luteo/a</td>
<td>luteolin, quercetin, ramnetin, campherol</td>
<td>yellow</td>
</tr>
<tr>
<td>Rillus coriaria</td>
<td>ellagic acid quercetin</td>
<td>graphite black</td>
</tr>
</tbody>
</table>

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**Vegetable**

- Vaccinium myrtillus: Exemplary vegetable used for colouring textiles and chemical compounds [13].
- Rubia tinctorium: In medieval and from the 2nd century. It confirms the premise that there was a very high level of wool manufacturing in the Roman period [8].
- Acrotostaphy/os urae ursi: Used for identifying raw materials.
- Alchemilla herba: Used for identifying raw materials.
- Bereroeris vulgaris: Used for identifying raw materials.
- Betula alba: Used for identifying raw materials.
- Equiseti: Used for identifying raw materials.
- Galium vennum: Used for identifying raw materials.
- Galia turbica: Used for identifying raw materials.
- Hyperici herba: Used for identifying raw materials.
- Lawsonia internis: Used for identifying raw materials.
- Polygonum avicula/are: Used for identifying raw materials.
- Quercus robur: Used for identifying raw materials.
- Rezeda luteo/a: Used for identifying raw materials.
- Rillus coriaria: Used for identifying raw materials.
- Sorbus aucuparia: Used for identifying raw materials.
- Vaccinium myrtillus: Used for identifying raw materials.
This method can be used to analyse some other aspects of historical textiles. For instance, it was successfully applied to evaluate the state of degradation due to light-ageing in historical woolen threads from collections of Flemish tapestries by comprehensive analysis of some characteristic features of IR spectra [10].

**Atomic absorption spectroscopy (AAS)**

Atomic absorption spectroscopy AAS can be used to determine metals (Zn, Cu, Ag, Au, As) and their concentration in samples. It is a cost – effective method for studying inorganic constituents and contaminations. The method can be applied to analyse the decorative metal threads often used in historical laces and embroidery.

The AAS method uses a phenomenon discovered at the beginning of 19th century by Fraunhofer. The radiation which is characteristic for elements is absorbed at the same rate as their emission. Samples (water solutions) are inducted at a low temperature (1000–4000 K) and illuminated by a lamp emitting resonant radiation. There is a specific lamp for each element (multielement lamps are sometimes used, for instance [Ca,Mg,Al], [Fe,Cu,Mn], [Ch,Pb,Zn,Sn]). This method is very sensitive, allowing the determination of minute quantities of elements: silver – 0.001 ppb; copper – 0.005 ppb; cadmium – 0.0002 ppb.

The method was used to analyse chasuble found during the restoration of the Collegiate Church in Tum, Poland. Figure 8 presents fragments of preserved embroidery made with the use of different kinds of metal-warped threads, pearls and sequins. While these elements were easy to determine, threads in the form of wire covered by the green rot, as presented in the figure, were more difficult to identify. Because of green rot, they were initially identified as copper wire. The thread sample was mineralised (in a microoven) to remove all organic contaminants. The thread sample was mineralised (in a microoven) to remove all organic contaminants.

**Identification of colour**

Archaeological textiles are usually, with very few exceptions, in different shades of brown, resulting from many factors, like the immersion of dyes and the presence of tannin in the soil. The original colour, however, was different. They could have the original colour of the raw material used – flax or wool, but in many cases they were dyed.

Analysing archaeological textiles with an optical microscope can sometimes notice that some fibres have a different hue. However, this way we can recognise the colour red, but we can’t determine what kind of dyes were applied in the fabric finishing. For this purpose the methods of chemical analysis should be applied.

Archaeological textiles were dyed using different mixtures of extracts of some vegetables and animals. All these dyes contain different chemical compounds, which we need to identify to determine the colour.

**Table 3** presents exemplary colouring vegetables, the chemical compound they contain, and the colour they give [13]. Among animal dyes one of the oldest is purple, which is obtained from types of crab (Marex brandaris, Marex trunculus) mainly found in Mediterranean countries. In Poland insects of the type Porphyrophora polonica and Porphyrophora hameli were commonly used, containing carmine acid and kermes vermicio.

Different analytical approaches are used to identify natural dyestuffs in archaeological textiles. The most popular methods are thin layer chromatography (TLC) and high performance liquid chromatography (HPLC). Liquid chromatography allows to determine the kind and concentration of the sample components.

The analysis starts from the preparation of a microextract, separating the mixture of the components analysed and impurities from the object. The extract is then subjected to microfiltration to separate the fractions which can contaminate the HPLC column. The sample is injected through a special dosage valve. The liquid is pressed through a pump under a pressure of 100-300 atmospheres. The separated mixture then reaches the detector (for instance UV, refraction, MS). The basic parameter of identification is the time of retention in the given system of solvent polarity. Identification of dyes consists in comparison between chromatograms of the mixture of chemical compounds, which we can use as the standard, and chromatograms obtained for extracts from archaeological fabric.

This method can be applied in both historical and archaeological textiles. HPLC was used in the analysis of the fabric presented in Figure 9a in order to reconstruct its original appearance. Tannin was identified in darker threads, while in light ones no dye was found [14]. It allowed to determine the woven pattern, as presented in Figure 9b.

However, sometimes the absence of dyes which was stated during the test does not mean the fabric was not dyed. After excava- tion, archaeological textiles need to be cleaned and are subjected to many conservation treatments to remove the soil, microflora and some products of decay. The radical conservation process can easily remove surviving residues of dyes from the fabric.

The other methods used to identify and analyse the colour of textiles are photoacoustical spectroscopy, laser-induced fluorescence and reflection spectra.

While the colour of a large majority of archaeological textiles has completely changed, in the the case of historical textiles, it has usually only paled, and the original colour can still be found on the left side of the fabric or under the seam. It can then be determined using Munsell Colour Standards, established at the beginning of 20th century. They can not only be applied for the assessment of the colour, but also in the calibration of printers, monitors or other devices [15]. This kind of data should be used in object documentation, but it can be also very useful in comprehensive analysis or in manufacturing a fabric replica.
Analysis of dyes can also be very helpful in the reconstruction of textiles as well as in the identification of the origin of fabric [16].

**Conclusions**

The main problem hindering the proper analysis and documentation of archaeological textiles is a lack of co-operation between scientists dealing with different aspects of these objects – archaeological, artistic, historical and technological. The latter includes the examining of manufacturing methods and raw material used, which is fundamental for proper identification of the object, its origin and dating. One of the reasons for such a situation is that there is relatively little knowledge about the research potential of contemporary chemical analysis that can be applied in the case of archaeological objects. There is also a lack of awareness that some conservation treatments, eliminating some substantial elements, make further analysis of the object impossible. A good example is the identification of dyes, or the analysis of archaeological context. Cleaning of a fabric can result in removing minute quantities of dyes, mordants, metals and their compounds. Thus a two-stage analysis is postulated – before and after the conservation.

Proper and detailed analysis can be very helpful in the conservation of fabrics. The data obtained can be used in works on the reconstruction of archaeological textiles. In the case of historical textiles, it allows proper identification of the workshop and, thus, can be very helpful in determining a fabric’s age and origin.

**Editorial note**

- The string was found in Jartypory, pl. 2, by Jacek Andrzejowski form the Archaeological Museum in Warsaw in grave no 269, inv.1534.

- The fabric was found in the male grave 1 of mound 3, dated for B2/C1 phase of the roman period in Gronowo, Pomerania.

**References**


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Received 6.05.2008 Reviewed 4.07.2008