The “Coptic” textiles of the “Museo Egizio” in Torino (Italy): a focus on dyes through a multi-technique approach

The "Coptic" textiles of the Museo Egizio di Torino: a focus on dyes through a multi-technique approach

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Abstract

The Coptic textile collection of the Museo Egizio di Torino has been the object of a broad project aimed at investigating the production techniques, at documenting the conservation state and at reconsidering the attributed age. The collection was also analysed by non-invasive and micro-invasive techniques with the aim of detecting the dyes that have been employed to obtain the colours, in order to complete the set of technological information available for each textile. The data collected in the present work have been compared with published results from other Coptic textiles collections, with the aim of highlighting a possible link between age of the textile and the dyes that were employed. Moreover, the combined use of spectroscopic and chromatographic techniques allowed us to compare the results for the non-invasive and the micro-invasive approaches, and to go deeper into the dyeing technology by detecting unexpected combinations of dyes. In particular, the use of a double dyeing with madder and Indian lac dye was revealed in some Roman-Byzantine and Byzantine textiles.

Keywords: Coptic textiles; dyes; HPLC-DAD-MS; FORS; non-invasive analysis.

Introduction

Textiles are intrinsically perishable materials, therefore they rarely survive in the archaeological record. A noticeable exception is represented by Egypt, where the sandy soil and the peculiar burial rituals have favoured the conservation of a large number of textiles, which constitute a unique testimony of spinning, weaving, dyeing and textile iconography over millennia.

As reported by Herodotus, flax has been used for a very long time in Egypt as the exclusive fibre for textiles employed in funerary practices (Lucas 1934, p. 140). After the Roman conquest of Egypt, the Pharaoh's religion was increasingly substituted by the spreading of Christianity and consequently new funerary rituals were gradually adopted; the bodies were buried fully clothed, sometimes even wearing many layers of clothes, with further dresses and other textiles sometimes added in the grave (De Moor et al. 2008; Guidotti 2014). Cloths and furnishing fabrics recovered from these burials show decorations obtained by mastering the loom techniques, with richly coloured wool threads employed in addition to uncoloured flax. Dyes are in fact easily fixed on wool and a larger set of dyes can be employed to impart a variety of colours (Cardon 2007).

Textiles from clothes and furnishing fabrics found in burial environments in Egypt and dated from the Roman times to the medieval period (from 1st BC to 13th century AD) are usually indicated as a whole as "Coptic" textiles. The term Coptic is actually rather vague; it was derived from the word used by the Islamic conquerors to indicate the indigenous Egyptians, and in the case of the so called Coptic textiles, the word is only partially related with provenance, age or religion. In fact, some of the textiles found in Egyptian tombs were almost certainly imported, the time-span of the so called Coptic textiles extends over more than a millennium and these textiles show features from both the Christian and the Islamic tradition (Carroll 1986; De Moor 2008). Nevertheless there is a general understanding of what people can expect when talking about Coptic textiles. Therefore the term is used here henceforth with quotation marks, to

stress the fact that it encompasses the variety of terminology approaches that have been used in the literature to indicate these textiles.

"Coptic" textiles began to appear in Europe in 17th century as curiosities and from that time onwards a vast amount of these textiles from tomb pillages, as well as from rudimentary archaeological expeditions such as the famous one of Albert Gayet at Antinoe (Gayet 1897), started to be available on the market. Thousands of such textiles reached Europe, particularly during late 19th and early 20th century (Carroll 1986; Rutschowscaya 1990). Unfortunately, for the majority of them, the information related to provenance and age was definitely lost. Moreover, coloured garnishments were normally cut out from larger textiles discarding the other parts and variously combining the fragments in order to obtain "new" and more attractive objects for the market (Carroll 1986; Antelo et al. 2011; Borrego and Vega 2015). As a consequence, the original use of the textile is sometimes difficult to recognize.

Presently, many Museums and private collections include "Coptic" textiles, mainly as fragments. For the majority of them the production date, or at least the assignment to historical periods such as Roman, Byzantine or Islamic times, is obtained according to stylistic features, while radiometric dating (^{14}C) have been only sporadically employed to accurately reveal their age (De Moor et al. 2008).

The "Coptic" textile collection of the Museo Egizio di Torino encompasses 248 textiles (Donadoni Roveri 1987). Some of them were excavated in the first decade of the 20th century in El Ashmunein (ancient Hermopolis) during an archaeological mission leaded by the director of the museum Ernesto Schiaparelli. The excavation was actually focussed on the rescue of Greek papyri, therefore only a small number of textiles (about 40) was recovered.

The other textiles were purchased or received as gifts between the last decade of the 19th century and the first decade of the 20th century. For these items the provenance is unknown or uncertain: The museum's inventory list of acquisitions mentions Deir Mari Girgis, Antinoe or Akhmim as possible sources for some sets, whereas for most of the textiles the indication of the archaeological context is missing.

The collection encompasses furnishing textiles (carpets and blankets), some tunics and accessories such as wraps, bags and headdresses. Many textiles of the collection are decorative bands (*clavi*), rings/ovals (*orbiculae*) or squares/rectangles (*tabulae*) which were cut out from larger textiles.

The majority of the decorations were produced using the tapestry wave technique, in which wool decorations are woven into the surrounding linen on the flax warp threads. Some decorations were obtained by the flying thread technique, in which a second shuttle is used to insert an extra flax weft thread into the fabric (Casini e Guidotti, 2014, De Jonge and Verhecken-Lemmens 1993).

104 textiles show monochrome wool decorations obtained in tapestry wave, while the others show a richer variety of colours. The iconography of the decorations can be subdivided into four major themes: a) geometric (purple or red, with light linen threads employed to obtain the pattern by flying tread brocading), b) plants motifs (such as flowers, buds, racemes, leaves or fruits); c) animals (a large variety is represented) and d) human figures. Some examples of the themes are reported in Figure 1.

The age of the textiles was established by comparing iconography, style and weaving techniques. Only one tunic, which is not considered among the present investigation and is discussed in a separate paper (Ferrari et al. 2015), was dated with ^{14}C. In order to give here an indication of the date, the following subdivision related to historical events has been adopted: Roman, Byzantine, Islamic. The beginning of the Roman period is set by 30 BC, when Egypt become a Roman province, and the end by 395 AD (death of Theodosius I). Byzantine period started with the subdivision of the Roman Empire after the death of Theodosius in 395 AD and ended with the Islamic conquest of Egypt in 642 AD. The Islamic period started in 642 AD and concluded with the Ottomans conquest of Egypt in 1500 AD. The collection of the here considered "Coptic" textiles encompasses items from all these periods. Figure 2 reports the textiles subdivided into five groups (Roman, Roman-Byzantine, Byzantine, Byzantine-Islamic, Islamic) according to their indicative age.

The amazing brilliant colours of "Coptic" textiles were obtained by natural dyes from the plant and the animal kingdoms (Cardon 2007) and have been mainly revealed by the chemical investigation of the textiles. Vat, mordant and direct dyes were exploited. Mainly proteinaceous fibres (normally wool) were dyed, whereas vegetable fibres (mainly flax) were normally bleached and used exploiting their natural colour. Weld (*Reseda luteola*) was largely employed as a source of yellow dyes. Luteolin and apigenin are the main colouring chemical species in weld (Peggie et al. 2008). Weld was employed alone to obtain yellow, or combined with other dyes to obtain other colours and shades such as brown, orange and green. Roots of plants of the *Rubiaceae* family, collectively indicated as madder, were the largely employed to obtain anthraquinone red dyes. Alizarin and/or purpurin are the most abundant (marker) molecules for madder, in addition to a large set of minor anthraquinononic compounds (Darkssen and Van Beek

2002). High-quality anthraquinone red dyes were also obtained from few species of scale insects such as kermes (*Kermes vermilio*), cochineals (*Porphyrophora polonica* and *Porphyrophora hamelii*) and Indian lac (*Kerria lacca*) (Wouters and Verhecken 1989) . The use of specific insects is recorded in the textile, as each family shows characteristic dyes. Kermesic acid is the main red dye from kermes, carminic acid characterises reds from cochineals and laccaic acids are obtained from Indian lac. Blue was obtained by vat dyeing with woad (*Isatis tinctoria*) or indigo (*Indigofera* spp.) (Coocksey 2007). Both woad and indigo are natural sources of indigotin, which is the main blue colouring molecule. The possibility of recognizing woad from indigo as the natural source of indigotin in "Coptic" textiles is linked to historical evidences and it is still not possible to distinguish them by chemical analysis with the available analytical methods. Woad or indigo were also used to obtain purple by dyeing the same fibre in successive baths of red and blue, although purple was also obtained by "true" purple: mono and di-brominated derivatives of indigotin from sea snails of the *Muricidae* family (Cooksey 2001).

In addition to the above reported dyes, which are found extensively in "Coptic" textiles, analytical evidences revealed the use of further natural sources for dyeing, such as tannins for brown, safflower and brazilwood for red and turmeric for yellow (Cabrera and Rodriguez 2007).

The colours of "Coptic" textiles have captured the interest of scientists, who have variously approached the determination of the colouring molecules and the recognition of the natural dyes that were originally employed to colour the fibres. The first work on this subject was performed in 1935 (Pfister 1935) employing chemical spot-tests. Thin layer chromatography has been also employed for the investigation of dyes in "Coptic" textiles (Cabrera and Rodriguez 2007), although more recently the preferred analytical technique for this topic has been high performance liquid chromatography (HPLC) coupled with photometric, spectrophotometric and/or mass spectrometric detectors (Wouters 1985; Wouters 1993; Wouters 1994, Wouters et al. 2002, Wouters et al. 2008, Rosemberg 2008, Petroviciu et al 2010, Abdel-Kareem et al. 2010). Some authors have considered "Coptic" textiles as a case-study for the comparison of UV-Vis, fluorescence and mass spectrometry detectors in HPLC detection of natural dyes (Orska-Gawrys et al. 2003; Surowiec et al. 2003; Szostek et al. 2003; Trojanowicz et al. 2004).

"Coptic" textiles have also been employed to test new-developed, high sensibility analytical methods for dyes detection. In particular, madder was detected by Surface Enhanced Raman Spectroscopy with laser photoreduced silver nanoparticles (Jurasekova et al. 2010) on a 6^{th}-8^{th} century AD (i.e.: byzantine) "Coptic" textile.

The "Coptic" textile collection of the Museo Egizio di Torino has been the object of a broad investigation project (Borla 2013) where many tasks have been performed to gain a throughout picture of the collection. Textiles fibers, waving techniques and dyes were investigated, the conservation state was documented and the attributed age was reconsidered exploiting stylistic, iconographic and technological match with other textiles that have been recently dated. In this task, textiles dated by the ^{14}C method were preferred as a bench for the match search.

The present paper focuses on one specific aspect among the overall investigation on the collection: the detection of dyes that were employed to obtain the colours. Dyes analysis was performed on 233 textiles with the aim of completing the set of information on stylistic, iconographic and technologic aspects related to each textile within the collection.

The textiles were preliminary subjected to a non-invasive screening by portable fiber optics UV-Vis diffuse reflectance spectrophotometry (FORS) and portable fiber optics fluorimetry (FL), which were employed sequentially on a same analytical spot. An overall general picture on the dyes was obtained by means of the non-invasive approach by performing a large number of analyses on the same object and by combining the information obtained from each of the two spectroscopic techniques. Moreover, the non-invasive survey allowed us to focus the sampling on few representative textiles. 32 micro-samples were then taken in order to obtain a more in-depth view on the dyes through high performance liquid chromatography coupled with diode-array spectrophotometric and mass spectrometric detection (HPLC-DAD-MS).

The information on the colourants found in the "Coptic" collection of the Museo Egizio di Torino was compared with published data obtained for other "Coptic" textiles collections (Wouters 1993, Cabrera and Rodriguez 2007; De Moor

2007; Bénazeth 2007; Cortopassi and Verhecken-Lammens 2007; Fluck and Malck 2007; Paets gen. Schieck 2007; Pritchard 2007; De Moor et al. 2008; Mérat 2013), with the aim of highlighting a possible link between age of the textile and the dyes that were employed, following the approach already suggested by Verhecken (2007)

As a whole, in the present work the combined use of FORS, FL and chromatographic techniques allowed us to highlight strong and weak points of the non-invasive and the micro invasive analytical approaches, to go deeper into the old dyeing technologies and detect unexpected combinations of dyes.

Materials and methods

Materials

Dimethylsulfoxide (DMSO), formic acid (FA), ethylenediaminetetraacetic acid disodium salt (EDTA), hydrochloric acid 37% w/w (HCl), methanol (MeOH) and acetonitrile were purchased as analytical grade products from Sigma Aldrich (St. Louis, MO. USA). Ultra-high quality water (electrical resistivity > 18 MΩ cm) was employed for aqueous solutions and was obtained by a Milli-Q system, Merk Millipore (Darmstat, Germany). All the glassware was washed with a non-ionic surfactant solution, soaked with UHQ water and treated at 400°C for cleaning.

The acidic extracts from step 2 and 3 were evaporated to dryness, favouring the removal of the solvent by keeping the tube at 40 °C and by blowing a gentle stream of nitrogen above the surface of the solution. The residue was than dissolved in the DMSO solution from extraction step 1, cleared in the centrifuge and injected in the chromatographic system.

For one sample, for which the non-invasive analysis indicated the use of purple from sea snails, only step 1 was employed for the extraction of the dye (Mantzouris et al. 2014).

An Ultimate 3000 Dionex, Thermo Scientific (Milan, Italy) HPLC instrument coupled with a Surveyor PDA-UV Thermo Scientific (Milan, Italy) detector and through an ESI source to an LTQ Orbitrap Thermo Scientific (Milan, Italy) mass analyzer were used.

The separation was achieved with a Luna C18(2) column (150 × 2.1 mm, 3 µm particle size, Phenomenex, Bologna, Italy). Acetonitrile (solvent A) and formic acid 0.15% (solvent B) were used as eluents in a gradient program which started with 10/90 to 100/0 A/B in 60 minutes. The injection volume and the flow rate were 10 µl and 200 µl min^{-1}, respectively.

Fibre optics UV-Visible diffuse reflectance spectrophotometry (FORS)

FORS analysis (988 spectra were recorded and processed) was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source were connected with fibre optic bundle to an FCR-7UV200-2-1,5x100 probe. In this configuration, light was sent and retrieved by the bundle set at 45° from the surface normal, thus excluding specular reflectance. The spectral range of the detector was 200-1160 nm, nevertheless, due to poor blank correction on both the extremes of the range, only the range between 350 and 900 nm was considered; as per the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2,4 nm calculated as full width at half maximum (FWHM). Spectra were referenced against the WS-2 reference tile provided by Avantes. The diameter of the investigated area on the sample was 1 mm, obtained by setting the distance between probe and sample at 1 mm. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The whole system was managed by the AvaSoft 8 software, running under Windows.

Fluorimetry (FL)

An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to measure molecular fluorescence spectra (836 spectra were recorded and processed). The instrument is equipped with a 365 nm Jaz-LED internal light source; a QF600-8-VIS/NIR fibre optic probe is used to drive excitation light on the sample and to recover emitted light. The spectrophotometer worked in the range from 190 to 885 nm; according to the features of monochromator (200 µm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in diameter, obtained by setting the sample-to-

probe distance at 1 mm. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system was managed with SpectraSuite software running under Windows.

HPLC-DAD-MS analysis

32 samples were obtained, detaching small threads from textiles that were not further damaged by the sampling. The samples were inspected under an optical microscope in order to detect possible contamination by exogenous materials. Evident contamination was removed by surgical tweezers in this step. About 1 mg of sample was treated in a centrifuge tube to extract the colourants. A three-steps procedure was adopted, which was set up according to the literature (Manhita et al. 2011, Mantzouris et al. 2014, Valianou et al. 2009) in order to sequentially extract the various chemical families of dyes that might have been present in the samples. Centrifugation was employed to clear the extracts and was performed at a relative centrifugal force of 36 000 for 10 min. The samples were treated as follows:

Extraction step 1. Performed with 500 of DMSO (15 min, 95°C) followed by centrifugation; the supernatant solution was then transferred into a separate tube.

Extraction step 2. The residue from step 1 was treated with 200 µL of FA and 200 µL of 1:1 (v/v) MeOH:H2O (90°C, 5 min). Further 400 µL of 0.5 mM EDTA were then added (90°C, 10 min). The solution was cleared by centrifugation and transferred into another clean tube.

Extraction step 3: The residue from step 2 was treated with 500 µL of 2:1:1 (v/v/v) HCl:MeOH:H_2O (90°C, 15 min) and the cleared solution was added into the tube containing the solution from step 2.

The acidic extracts from step 2 and 3 were evaporated to dryness, favouring the removal of the solvent by keeping the tube at 40 °C and by blowing a gentle stream of nitrogen above the surface of the solution. The residue was than dissolved in the DMSO solution from extraction step 1, cleared in the centrifuge and injected into the chromatographic system.

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An Ultimate 3000 Dionex, Thermo Scientific (Milan, Italy) HPLC instrument coupled with a Surveyor PDA-UV Thermo Scientific (Milan, Italy) detector and through an ESI source to an LTQ Orbitrap Thermo Scientific (Milan, Italy) mass analyzer were used.

The separation was achieved with a Luna C18(2) column (150 × 2.1 mm, 3 µm particle size, Phenomenex, Bologna, Italy). Acetonitrile (solvent A) and FA 0.05% (solvent B) were used as eluents in a gradient program which started with 10/90 to 100/0 A/B in 60 minutes. The injection volume and the flow rate were 10 µl and 200 µl min^{-1}, respectively.

The LC column effluent entered the ESI source with nitrogen as sheath and auxiliary gas. The heated capillary temperature was maintained at 300 °C. The other main parameters adopted were: source voltage was set to 4.5 kV, capillary voltage 21.00 V, tube lens 80 V for positive ionization mode; source voltage 3.5 kV, capillary voltage 18.00 V, tube lens 70 V for negative ionization mode; all others parameters were optimized for maximum sensitivity. Full scan spectra were acquired in the range of *m/z* 200-1100. High resolution spectra were acquired with a resolution of 60,000 (500 *m/z* FWHM) and the mass accuracy of recorded ions (vs. calculated) was ± 2 millimass units (without internal calibration). The UV-Vis spectra were acquired by the DAD in the range 200-900 nm.

The identification of the dyeing molecules was performed according to their spectroscopic features (revealed by the DAD) and through mass spectra. In some cases, the concentration of the dyes was too low to be detected by the DAD, although detectable mass spectra were obtained. For some marker molecules (purpurin, alizarin, laccaid acids A, B, C, D, carminic acid, indigotin) retention time match was also adopted by preparing standard solution of pure molecules as a reference. A reference solution of kermesic acid was obtained by treating a kermes lake pigment with HCl:MeOH:H_2O (2:1:1 by volume) at 90°C for 15 min. The obtained solution was evaporated to dryness and the residue was dissolved in DMSO. The features of the dyes detected here by the chromatographic analysis are reported in Table 1.

Results and discussion

The overall results obtained for dye analysis on the 233 textiles of the collection are reported on-line as electronic supplementary material (Table S1).

Non-invasive analysis

FORS and FL spectra were recorded from all the different colours in each textile. In FL measurements, also the unbleached linen was considered, in order to gain signals that can be related to the uncoloured fibres.

FORS spectra allow us to detect some of the dyes in relation to specific spectroscopic features (Gulmini et al. 2013). In particular, indigotin has a characteristic absorption band with a broad maximum at 660 nm and was detected in all the blue samples. The absence of significant fluorescence signals, which are not evident with the excitation wavelength employed here for FL measurements, further confirms the assignment. Nevertheless the origin of the dye (from indigo or woad) cannot be ascertained.

Indigotin was also detected in green, purple, brown and black hues, indicating that vat dyeing was exploited in a sequence with mordant or direct dyes to obtain a variety of colours.

The combination of FORS and FL spectra enable us to distinguish, within the considered textiles, if anthraquinone reds from vegetal or animal origin were present. In the first case, the colour is obtained from alizarin and/or purpurin extracted from madder roots and fixed to the fibres by means of the mordant ions (normally Al^{3+}). The complex is detected in the reflectance spectrum thanks to the broad absorption band in the 450-600 nm region, which is the general characteristic of anthraquinone natural reds. Two characteristic sub-bands at 510 nm and 545nm enable the identification. Moreover, when excited under the 365 nm LED source, a characteristic maximum in the 575-585 nm range is expected. The textiles of the here considered collection, in which the spectroscopic features of madder have been highlighted by FORS, are subdivided into two groups according to the characteristics of the emission spectrum under the 365 nm LED source. Textiles representatives of these two behaviours are reported in Figure 3. Besides the peaks at 485 and 520 nm, that are related to the emission of the uncoloured warp threads, one group has a more blue shifted emission at about 570 nm, while for the other group the emission is centred at about 600 nm. This behaviour may be related to a different quantitative ratio between alizarin and purpurin, which has been employed to distinguish among different madder sources (Wouters et al. 2008). The topic has been further investigated by micro-invasive analysis and is discussed in the next section.

The spectroscopic characteristics of madder are distinct from those of other natural anthraquinone red dyes such as kermes, cochineal and Indian lac, which are obtained from scale insects. In particular, the dyeing with scale insects was recognized in the textiles considered here by the presence of two sub-bands at about 525-530 nm and 560-570 nm. Moreover, the fluorescence spectrum obtained using the 365 nm LED source shows a maximum at about 630 nm that further support the assignment.

The analysis also revealed the textiles in which red dyes from madder or from scale insects were used in a subsequent dyeing with indigo to obtain the purple colour. The resulting purple colour is extensively present in the collection, which encompasses a large number of purple *orbiculae* and *tabulae* in which elaborated geometric decorations are obtained with uncoloured threads added by a flying tread.

In only four textiles the purple colour was instead obtained by true purple from sea snails. True purple was detected by the characteristic absorption band at c.a. 520 nm. The indigotin band at 660 nm is also apparent in the spectrum, possibly as a consequence of debromination of the original dyes with the formation of indigotin (Cooksey 2001). The presence of mono- and di-bromoindigotin, which are characteristic of true purple from sea snails, is indirectly confirmed by the absence of detectable fluorescence signals under 365 nm excitation.

For other dyes, and for very dark areas such as black, the information given by the non-invasive approach is less robust. In particular, it has been previously demonstrated (Gulmini et al. 2013) that within the here considered spectral range the absorption characteristic of yellow dyes are not selective. Similarly, the behaviour of fluorophores in all the yellow textiles does not offer straightforward spectroscopic features for the identification of the dyes. The characteristic absorption bands of saffron at 440 and 470 nm were not detected in any among the considered textiles,

thus excluding the use of this dye in the examined items. Moreover, some spectra were tentatively assigned to an iron(III)-tannin complex employed to impart the brown colour.

In few cases, the spectroscopic characteristics of red, orange and blue areas were barely appreciable (in these cases a tentative attribution is given and is highlighted by a question mark in table S1) or were not visible at all (and therefore the identification was not performed).

As a whole, the non-invasive survey of the collection enabled the detection of red dyes from *Rubiaceae* (madder) and from scale insects both in red and in purple samples. In purple samples, the red dyes were used in subsequent dye baths with indigo/woad. The spectroscopic non-invasive inspection also enabled the recognition of true purple obtained by sea-snails. The spectroscopic features recorded by FORS on textiles dyed with madder, scale insects dyes, sea snails purple and indigotin, as well as those of textiles obtained by double-dying, are reported in Figure 4. The picture reports data as apparent absorbance (Aceto et al. 2014) in order to emphasise the absorption features of the samples. A more in-depth information about the specific species of scale insects (i.e.: kermes, Indian lac or cochineal) is not achievable by portable techniques; therefore, this aspect has been further considered by micro-invasive analysis.

Chromatographic insight

The use of HPLC-DAD-MS analysis allowed us to elucidate some points that were not fully understood after the non-invasive survey. In particular, our attention was focussed on the detection of yellow dyes, on the recognition of the scale insects dyes and on the definition of a possible relation between fluorimetry data reported in the above section and the alizarin-to-purpurin ratio in samples dyed with madder.

As for the yellow dyes, yellow (6 samples) and orange (3 samples) samples were considered. In all the samples, apigenin and luteolin were present as major dyeing compounds, and crysoeriol was also detected, thus revealing the use of weld in the considered samples (Peggie et al. 2008). In some samples, the glycosylated derivatives of apigenin and luteolin were also present. Alizarin and purpurin were detected in addition to the yellow dyes from weld, confirming the information obtained by the non-invasive analysis that revealed the use of madder as a source of the red dyes.

One sample (S2168) out of the four decorated with wool thread dyed with sea-snail purple was analysed and the attribution of the non-invasive analysis was confirmed. Moreover, indigotin (and trace levels of indirubin) from woad/indigo were detected in one black sample (S. 1734), for which the non-invasive survey was unable to give information on the dyes.

Three samples (namely S17312, S17474, 17491) were considered to define the scale insect species that were employed to obtain the colour. In these samples, the presence of laccaic acids A, B and trace levels of kermesic acid indicate the use of Indian lac (*Kerria lacca*) to obtain the colour (Wouters and Verhecken 1989). Nevertheless, also intense peaks of alizarin and purpurin were detected. By combing the spectroscopic data from the non-invasive analysis and HPLC-DAD-MS results, a procedure in which the fibres were firstly treated with madder and then in a bath of Lac dye to impart the final colour can be suggested. In fact, the non-invasive survey clearly detected signals from scale insects dyes, and not spurious signals deriving by the combination of signals from madder and scale insects. Therefore a sequence of dyeing baths seems more suitable than a single dyeing with a mixture of dyes to explain the experimental data.

Laccaic acids A, B (in this case without the presence of markers for madder) were also unexpectedly detected in a brown sample (S17463). Here the non-invasive analysis did not reveal the dye, and spectra possibly attributed to iron(III) complexes with tannins were obtained. Further investigation is needed on this sample, possibly considering alternative extraction and detection methods to reveal tannins (Trojanowicz et al. 2004; Lech and Jarosz 2011).

In one sample (namely S. 17426) data from the non-invasive analyses and the HPLC-DAD-MS determination are discordant. FORS and FL signals suggest the use of scale insects to obtain the red colour, although only signals of alizarin and purpurin were obtained from HPLC-DAD-MS analysis. Unfortunately, the low amount of sample did not allow us to treat further sample for HPLC analysis and therefore we are still not able to confirm, for this sample, the dyes that have been employed. This result may arise from the low amount of scale insect dyes that may be present in

the thread if a finishing dyeing was employed on madder dyed fibres. The chemical species that are detected directly on the textile by FORS may in fact fall under the instrumental detection limit in the solutions obtained after their extraction.

A further aspect that has been considered by HPLC-DAD-MS is the consistency of the two groups that can be obtained by considering the features of the fluorescence spectrum, as already indicated in the above section. 14 samples were considered: 6 showing an emission band centred at 570 nm (therefore a higher level of purpurin is expected) and 8 showing an emission band centred at about 600 nm (a higher level of alizarin is expected in these samples). The chromatographic separation confirms the presence of madder and the peaks of alizarin and purpurin were evident. The ratio between peak areas was calculated considering the signals from the photometric detector in the spectral range from 400 to 500 nm. Values from 0.03 (higher level of purpurin) to 1.67 (higher level of alizarin) were detected, but unfortunately the data were randomly linked to the position of the emission bands in the fluorescence spectrum.

Dyes in relation with age of the textile

As some dyes were not available locally and were imported into Egypt for textiles dyeing, the appearance of specific dyes might have been related to the opening of new commercial contacts in specific periods or to the introduction of new productions. This topic has been discussed by A. Verhecken (2007) considering 450 textiles. Among them, 66 were dated by radiocarbon. In his work, Verhecken suggests specific time intervals for the use of some dyes (namely: true purple from sea snails, kermes, cochineal, Indian lac, brazilwood and safflower), while others (tannins, indigo, weld and madder) have been used from Roman to Islamic periods.

Verhecken's (2007) data suggest that the use of true purple declined by 500-550 AD and that Indian lac was possibly introduced by the Islamic conquerors replacing kermes. Moreover, cochineal appeared by the end of 4th century until about 650 AD. In general, dyes from scale insects appeared at the beginning of 5th century. These guidelines were obtained by considering only data obtained on textiles dated by ^{14}C, and found only partial overlapping with the picture that emerged if textiles with indirect dating are considered.

Such an approach was also considered for the Coptic collection of the Museo Egizio di Torino. The textiles in relation to the dyes (and their combinations) and to the assigned age of the textiles are reported in Figure 5, focussing on red and purple hues, which are more promising for dating purposes. Figure 5 shows that the results obtained from the Coptic textile collection of the Museo Egizio di Torino partially confirm the picture that emerged from Verhecken's data aiming at highlighting a possible connection between the date of the textile and the dyes employed to obtain the colour. In particular:

- 38 out of 40 textiles from the Museo Egizio di Torino are in agreement with previous data indicating that scale insects started to be used for dyeing in the Byzantine period. In two textiles attributed to the Roman period (namely S. 17473 and S. 17358) scale insect dyes were detected
- 3 out of 4 textiles are in agreement with a use of true purple from sea-snails mainly concentrated in the Byzantine period. One textile (namely S. 2169) is in fact attributed to Islamic times.

The HPLC-DAD-MS insight on dyes from scale insects does not support the hypothesis of the introduction of Indian lac after the Islamic conquest of Egypt; the dye was possibly already in use during late Roman and Byzantine periods as indicated by Lac detection in textiles S 17312, S. 17463 and S. 17491 attributed to Roman-Byzantine or Byzantine periods.

Conclusions

The collection of the Museo Egizio di Torino cannot be considered a representative (unbiased) set of textiles from the complete set of "Coptic" textiles presently owned by museums and private collectors; nevertheless it offered us the opportunity of systematically investigating a large set of textiles and of gaining information on dyes and on dyeing techniques.

The non-invasive analyses with FORS and FL highlighted textiles in which purple was obtained by sequence dyeing with red and blue dyes and textiles in which true purple from molluscs was instead used. Moreover, the use of scale insects to obtain red (and purple, if woad/indigo is also used) was detected by this analytical approach.

HPLC-DAD-MS analysis indicated that red from scale insects were obtained by employing Indian lac and madder, thus revealing a specific technique that was highlighted here in textiles considered for the micro-invasive analysis. As these

textiles were presently dated from the Roman-Byzantine to the Islamic period, a more straightforward dating performed by absolute dating techniques will be useful to better define the time boundaries (if any) of this particular dyeing procedure.

A systematic investigation on HPLC-DAD-MS procedures for extraction and detection of Lac dye in textiles would possibly clarify the mismatch that emerged in one instance between data obtained with the non-invasive techniques and data obtained by the micro-invasive approach.

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Captions to figures

Figure 1: Examples of the main decorative themes of the Coptic textiles from the Museo Egizio di Torino. 1-4: plant motifs (S. 17416, S. 1789, S. 17358 and S. 17435); 5-8: animals (S. 17437, S. 17416, S. 17435 and S. 17360); 9-12: human figures (S. 17416, S. 17370, S. 17415 and S. 17414).

Figure 2: Number of textiles assigned to groups of different age according to stylistic and technical features.

Figure 3: FL spectra for textiles dyed with madder. Two samples representatives of two different behaviours are reported. The dash-line spectrum shows an emission feature at about 570 nm, while in the solid-line one the peak is centred at about 610. The peaks at 485 and 520 nm are related to the emission of the uncoloured warp threads in both spectra.

Figure 4: FORS spectra representative of red and purple textiles dyed with: a) purple from sea snails; b) indigo/woad; c) scale insects and indigo/woad; d) scale insects; e) madder and indigo/woad; f) madder. Spectra are reported as apparent absorbance in order to better show the absorption features.

Figure 5: dyes employed to obtain the red and purple decorations in monochrome and polychrome textiles of the collection of the Museo Egizio di Torino in relation to their age. Numbers are the number of textiles assigned to the indicated period and dyed with the indicated dye (or combination of dyes).

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Table 1

Table 1: list of the compounds detected in this work by HPLC-DAD-MS in "Coptic" textile form the Museo Egizio di Torino. Spectrophotometric and mass spectrometric features are reported whenever detectable at the analytical conditions indicated in the text.
The mass spectra of mono- and di-bromoindigotin showed the characteristic signature of halogen atoms in organic compounds, with double and triple peaks, respectively, with 2 mass unit spacing.

Compound	**Abs λ_{max} (nm)**	**ESI positive mode $[M+H]^+$**	**ESI negative mode $[M+H]^-$**
Indigotin	247, 285, 326, 454, 607	263.08	261.07
Indirubin	252,286,334,615		261.07
6 bromoindigotin	248, 287, 341,443,602	340.67 342.67	338.97 340.97
6,6'-dibromoindigotin	254,289,303,345,595		416.88 418.88 420.88
Alizarin	203, 247, 277, 430	241.05	239.03
Purpurin	203, 255, 293, 480	257.04	255.02
Rubiadin			253.05
Xanthopurpurpurin			239.03
Laccaic acid A			536.09
Laccaic acid B			495.07
Laccaic acid D (Flavokermesic acid)			313.04
Kermesic acid			329.04
Apigenin	245, 266, 337,396	271.06	269.04
Apigenin glucoside		433.12	431.10
Luteolin	353,268,349	287.05	285.04
Luteolin glucoside	226,254,267,350	449.11	447.09
Crysoeriol		301.08	

Figure 1

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Figure 2

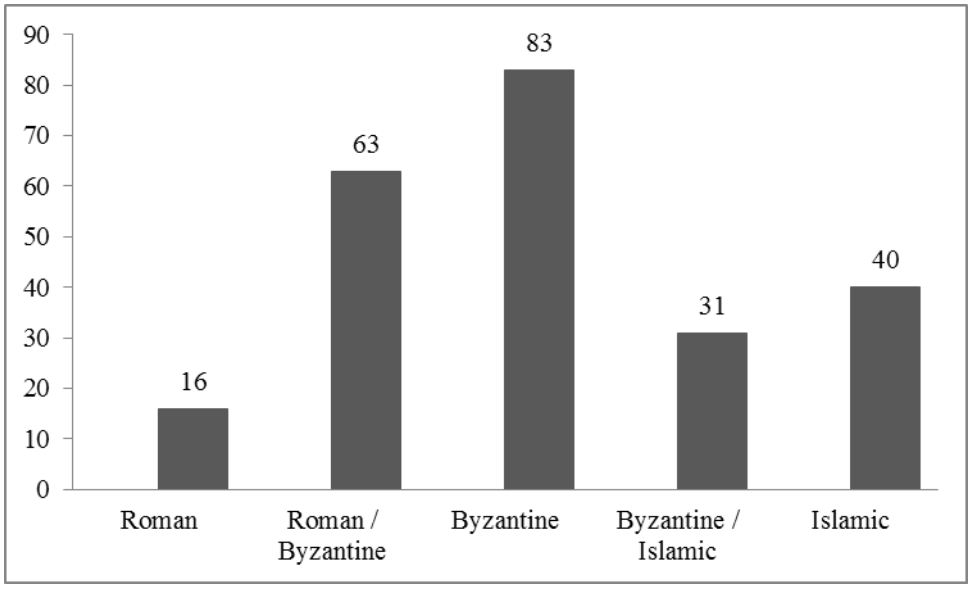

Figure 2: Number of textiles assigned to groups of different age according to stylistic and technical features.

Figure 3

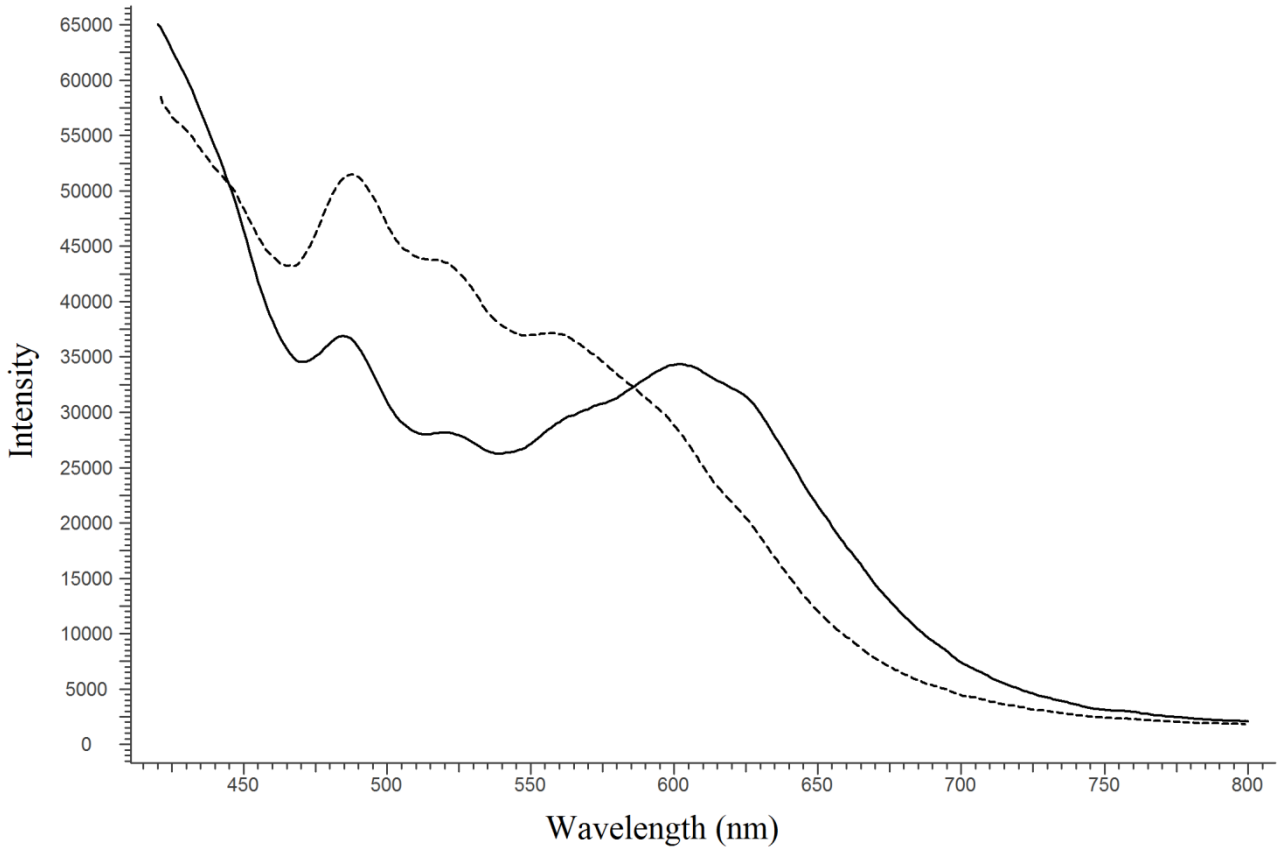

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Figure 4

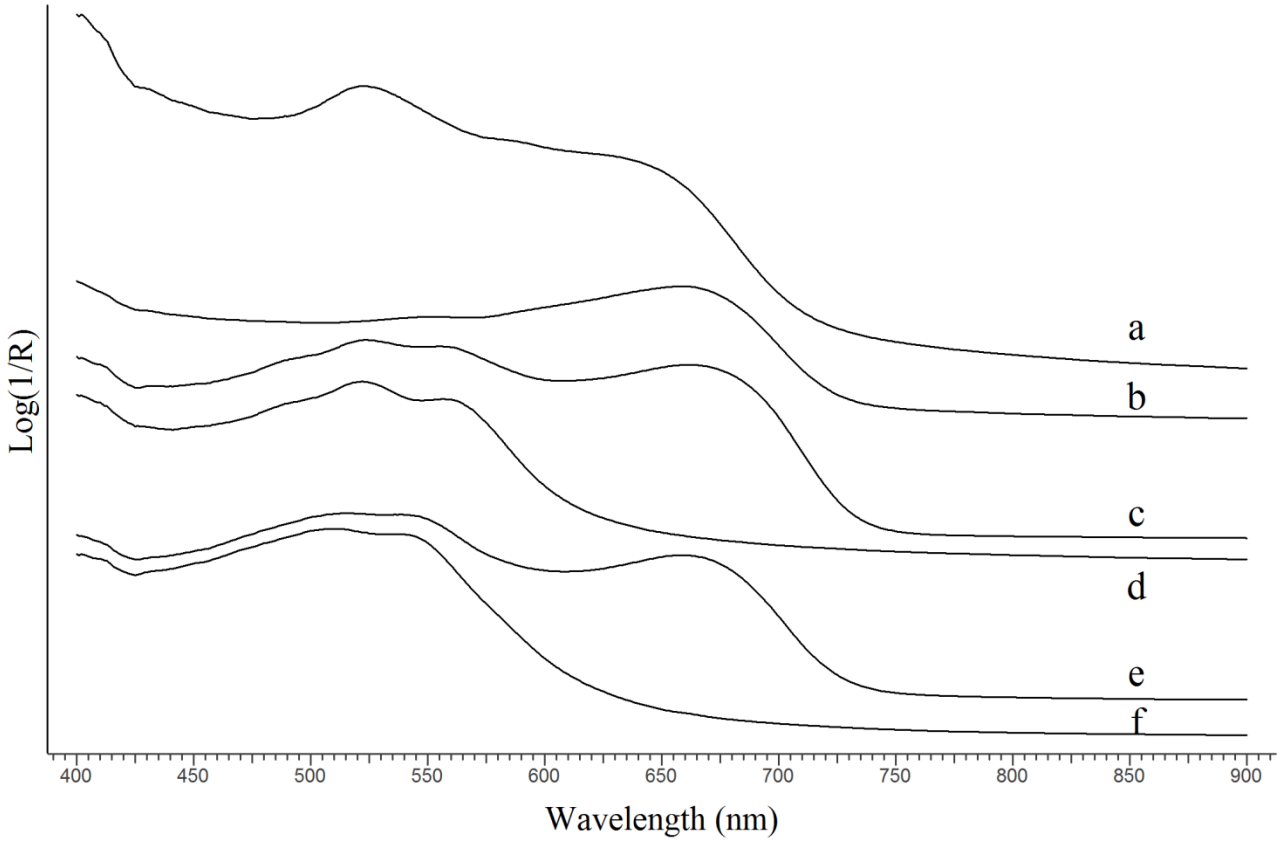

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Figure 5

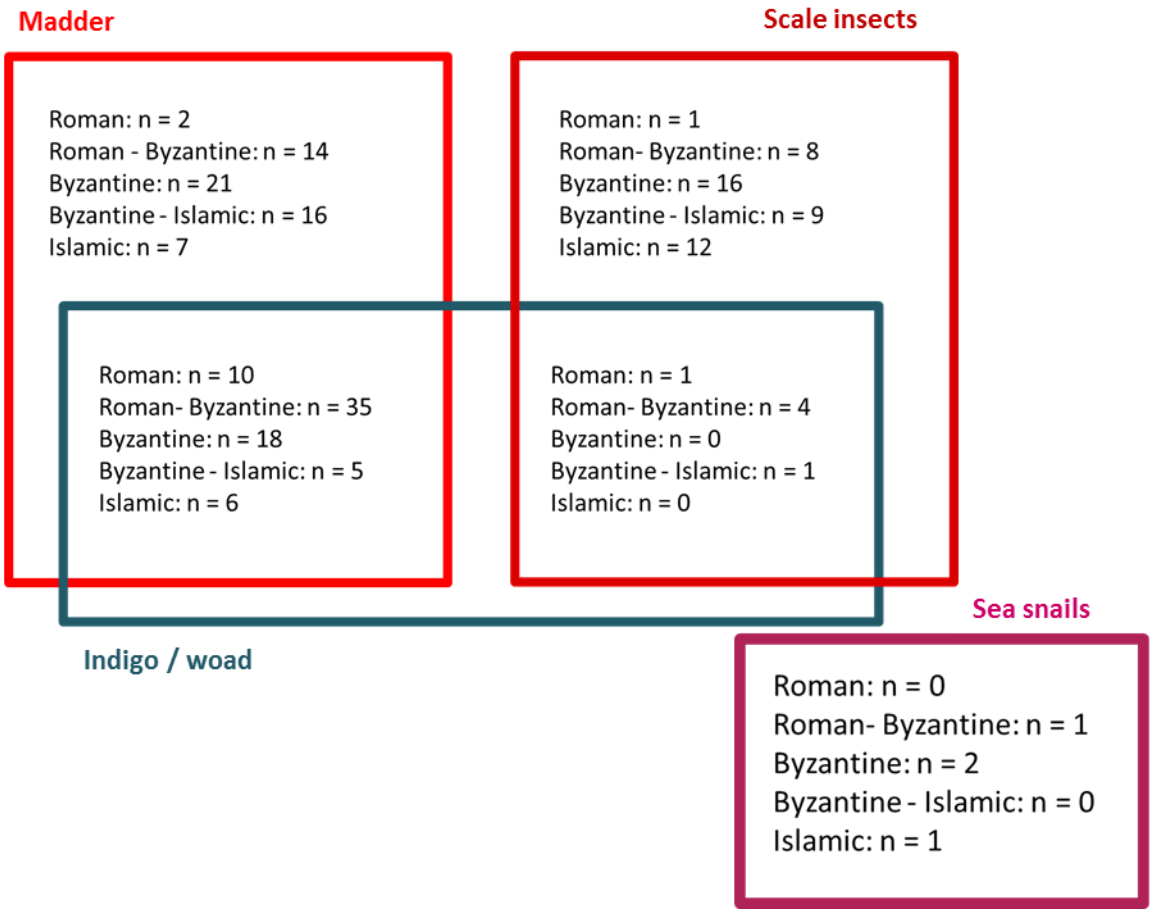

Figure 5: dyes employed to obtain the red and purple decorations in monochrome and polychrome textiles of the collection of the Museo Egizio di Torino in relation to the age of the textiles assigned by stylistic, iconographic and technological features. Numbers are the number of textiles assigned to the indicated period and dyed with the indicated dye (or combination of dyes).