

## 5. THE DYE ANALYSIS: PART 1

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The dye analysis was done as two separate reports, which is how the text is laid out. The tables have been combined for easier reference.

### 5.1 Summary

Eleven fragments of striped woollen textiles recovered from Siller Holes were analysed by high-performance liquid chromatography with photodiode array detection to identify any dye which may still have been present. Nine samples were found to contain traces of one, or a combination, of the indigoid, flavonoid and anthraquinoid compounds associated with natural dyestuffs. In some cases, these could be more specifically identified as indigotin (blue), luteolin (yellow) and carminic acid (red).

While it is not possible to identify the exact sources of the dyestuffs because of the widespread occurrence of these natural dye components, the study has nevertheless shown that the analysed textiles had been dyed. Further analysis of the two fragments found to contain carminic acid may reveal minor components which could show which variety of cochineal (European or Mexican) had been used. This information might assist with dating the finds.

### 5.2 Introduction

Fieldwalking at the lead mining site at Siller Holes, near West Linton in Peeblesshire, recovered a number of leather and fabric fragments. Some of the textiles were coloured (red, green, brown and black), striped and made from coarse wool. It has been proposed that these striped woollen fragments date from the late medieval period, perhaps imported into Scotland. The textiles may also have been made from recycled quality garments.

Samples were submitted for dye analysis by photodiode array high-performance liquid chromatography to determine whether the textiles had been dyed and if this revealed more about their provenance.

### 5.3 Experimental

#### 5.3.1 Sample descriptions

Fibres were viewed under a light microscope at ×80 magnification to describe the colours given in Table 5.

#### 5.3.2 High-performance liquid chromatography with photodiode array detection

Samples were prepared and analysed as described in Appendix 1. Full results can be consulted; they will be held with the original data, currently at the National Museums of Scotland Collections Centre prior to their being deposited in Canmore.

### 5.4 Results

Component retention times and spectra were compared with those for reference dyes. Table 6 summarises the data. Although several peaks appeared in the reagent blank chromatogram arising from sample preparation, these did not interfere with the dye components.

### 5.5 Discussion

A number of chemicals associated with natural dyes were detected and identified in the textile fragments from Siller Holes. More detailed assessments of the results follow.

#### 5.5.1 Anthraquinones

Anthraquinones are present in many plants and insects which produce red dyes. A compound in both Samples 5 and 9 gave a good chromatographic and spectral match with carminic acid, a major anthraquinone component of several historically important insect red dyes. As a trace level compound in Sample 10 showed spectral, but not chromatographic, similarity to carminic acid, it can only be concluded that an unspecified anthraquinone compound is present.

Until the importation of Mexican cochineal (*Dactylopius coccus*), both Polish cochineal (*Porphyrophora polonica*) and Armenian cochineal (*Porphyrophora hameli*), along with kermes (*Kermes kerria*), were the main sources of insect red dyes in western Europe (Wouters & Verhecken 1989).

Although more expensive, Mexican cochineal quickly established itself as a much better alternative to kermes and the European cochineals because of its superior dye content. This is reflected in historical accounts and testified to by dye analysis results for red-coloured quality 14th- to 17th-century European textiles, which show a distinct transition in the preferred insect red from European to American cochineal over this period (Hofenk de Graaff 1983; Wouters & Verhecken 1989; Cardon 1990: 345–78).

An analytical study of the anthraquinone content of historical insect red dyes has shown that different sources for these dyes may be identified from the relative ratios and presence of certain anthraquinone compounds (Wouters & Verhecken 1989). If the carminic acid detected in the Siller Holes samples was found to derive from Mexican cochineal, then the textiles, if European in origin, are almost certain to date from the late 14th century at the earliest. However, a European insect source for this red dye could indicate that the textiles are older. Unfortunately, none of the characteristic secondary dye components could be detected in either Sample 5 or Sample 9 of the Siller Holes textiles, and so it is not possible to classify the source(s).

The anthraquinoid compound detected in Sample 11 was chromatographically more similar to those present in plant, rather than insect, dyes, although it could not be identified conclusively.

#### 5.5.2 Indigotin

Indigotin was identified in Samples 1, 2, 3, 5, 8 and 10. This compound is the main colouring compound of woad (*Isatis tinctoria*), a plant indigenous to Europe, as well as Indian indigo (*Indigofera tinctoria L.*) and synthetic indigo. It is not analytically possible to distinguish between the two natural sources, or even between synthetic and natural sources, at present.

#### 5.5.2 Flavonoids, including luteolin

Analysis revealed that Sample 4 contained the flavonoid luteolin, one of the most widespread flavonoids found in yellow-producing dye plants. The two most popular western European yellow dyestuffs were weld (*Reseda luteola L.*) and dyer's greenweed (*Genista tinctoria L.*). Weld maintained its reputation as one of the best fast yellow colours for many centuries in western Europe until the advent of more light-fast and cheaper yellows, like quercitron bark, in the late 18th century.

Unfortunately, secondary flavonoids, such as apigenin and genistein, which could have enabled the plant source to be determined, were not detectable in Sample 4 from Siller Holes. An unidentified compound with a flavonoid-like UV-visible spectrum was detected in Sample 8.

Yellow and blue dyes were often combined to produce a reasonably fast green colour. Although Samples 1, 2 and 3 appeared green, no additional dye compounds besides indigotin could be detected. This may be for two reasons: (i) burial has given the fibres a yellow tinge through wool discolouration or absorption of tannins so that they appear green; or (ii) the yellow dye(s) have degraded and are no longer identifiable.

### 5.6 Conclusions

This preliminary study of textile fragments from Siller Holes has revealed that 9 of the 11 samples analysed contain traces of major chemicals relating to natural yellow, red and/or blue dyes.

The dyestuff sources can only be speculated upon because additional characteristic compounds could not be detected, but the most likely plants and insects to have been used were popular for many centuries.

Further analysis of larger quantities of red fibres from SH 118 (3) and SH 139 might reveal more chemical information which could help characterise the insect dye source.