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Searching for blue: Experiments with woad fermentation vats and an explanation of the colours through dye analysis

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ABSTRACT

The starting point for this research was the requirement to produce replicas of Iron Age textiles from Hallstatt in Austria using traditional methods. Three traditional processing and dyeing methods using woad (*Isatis tinctoria* L.) were successfully recreated in an iterative experimental process: dyeing with fresh leaves, with green and couched woad and with woad pigment. During these experiments, several colours other than the typical blue also emerged. The light fastness of all colours was fairly good. Dye analysis using high-performance liquid chromatography with photo diode array detection (HPLC-PDA) showed that the most predominant component in the blue samples was indigotin. The colours mint, purple, beige and green were achieved when indirubin and flavonoids appeared in higher concentrations. The composition of the woad-related components detected on dyed samples enabled us to retrace the dyeing methods used. Anthraquinones originating from madder (*Rubia tinctorum* L.) used in the madder-bran vat were also detected, but in different ratios to that of madder mordant dyeings. Further research is required to prove whether the components detected in reference samples can be used to identify woad dyeing or the use of madder-bran vats in historic/archaeological textiles. The ultra-violet–visible absorption spectra obtained by HPLC-PDA were used to calculate RGB values, which provide a better understanding of the colour observed.

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1. Introduction

In Europe, woad (*Isatis tinctoria* L., Fig. 1) has been used for millennia to dye blue. The earliest woad-dyed textiles in Europe to date have been found in the salt mine in Hallstatt, Austria and are up to 3500 years old, dating from the Bronze Age (1500–1100 BC) and Iron Age (850–350 BC). In 33% of the Bronze Age textiles and 58% of the Iron Age textiles analysed, indigotin, indirubin and isatin were detected by HPLC-PDA (high-performance liquid chromatography with photo diode array detection). These components clearly indicate vat dyeing, but do not enable a conclusion to be drawn on which plant species yielding indigoids was used. Due to the textiles' prehistoric context, it was most probably woad (Hofmann-de Keijzer et al., 2013).

The starting point for the research was the requirement to produce replicas of three Iron Age ribbons from Hallstatt, using traditional spinning, weaving and dyeing techniques, based on the analysis of the

dyeing and textile techniques of the Iron Age ribbons and experimental archaeology. Literature describing different techniques of woad processing and fermentation vats was therefore studied (Section 2). We tested a broad range of methods, irrespective of the historical time period for which they are documented, to develop hypotheses on possible prehistoric dyeing techniques (publication in preparation) and to find out whether and how the different techniques can be retraced through a dye analysis of reference samples. During these experiments, several colours other than blue also emerged.

This paper focuses on the following questions:

- (1) *How can blue be dyed using traditional woad dyeing methods in a quality suitable for reproductions?* The development of the method is described in detail, without concealing mistakes or failures, to enable others to build on these experiences.
- (2) *What explanations can be given for the intended and unintended woad colours?* Dyed reference samples were analysed using HPLC-PDA, which provided an explanation of the colour shades through the detected components.
- (3) *Is it possible to find any relation between the different processing/dyeing techniques applied and the dyes detected on the reference samples?* Additional components detected on the reference samples suggest that this may be possible.

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Fig. 1. Woad (*Isatis tinctoria* L.): (a) woad leaf rosette in the first year, (b) inflorescence, appearing in the second year, and (c) seeds. Pictures: © A. Hartl (a + b), © A. G. Heiss (c).

2. Review of woad processing and dyeing methods and selection of methods for the experiments

2.1. Dyeing with fresh leaves

Traditional methods of dyeing with fresh leaves (process description see Table 1, column A) are documented for *Indigofera* spp., *Polygonum tinctorium* Aiton, *Strobilanthes* spp. and *Marsdenia tinctoria* R.Br. (Cardon, 2007; Bühler, 1950; Leuchs, 1857a). These sources provide a summary of historical and ethnographic reports from Africa, Central America and tropical Asia.

Dyeing with fresh leaves of plants yielding indigoids is a different process than the typical vat dyeing. When the fresh leaves are soaked in water, the precursors are transformed into indoxyl. Adding an alkali maintains the necessary alkalinity to neutralise the acids produced during fermentation. The indoxyl penetrates the immersed textile material and after the textile is taken out again, the indoxyl reacts with oxygen and forms indigotin (Cardon, 2007).

For woad, traditional¹ techniques of dyeing with fresh leaves are not documented in the literature we analysed. It is, however, quite possible that methods with fresh leaves also existed for woad, as dyeing with fresh leaves is considered to be a simple and very ancient process (Cardon, 2007; Bühler, 1950; Leuchs, 1857a). In our experiments, methods known from other plants were therefore adapted for woad.

2.2. Techniques to preserve the dye

To gain a storable and tradable form which enables the dyeing to be done independently from harvesting time and the place where woad is cultivated, woad leaves were processed: either into woad balls and couched woad (the typical technique of the European Middle Ages, Table 1, column C), or by the extraction of woad pigment, a process developed in the 19th century analogous to the indigo² extraction from *Indigofera* plants (Table 1, column D). Besides the transformation of the precursors contained in the fresh leaves into indigotin, these processes also provided a concentrated form of the dyestuff (Cardon, 2007).

Much historical, experimental and natural scientific research has been conducted on these techniques: the medieval technique of processing woad into balls, couching and dyeing in woad vats was successfully reconstructed for the first time by John Edmonds (Edmonds, 1993; Edmonds, 1998a; Edmonds, 1998b). There are annotated translations of original medieval dyeing recipes available (Cardon, 1992a; Cardon, 1998; Cardon, 1992b). The formation of indigotin during medieval processing methods has been identified as a microbiological process (Ewerdtwalbesloh and Meyer, 1998). The content of precursors and indigotin in the different processing steps has been quantified (Kokubun et al., 1998). The bacteria responsible for the reduction of indigotin in the woad vat have been identified (Padden et al., 1999; Padden et al., 1998; Nicholson and John, 2004). The 19th century methods of woad pigment extraction (e.g. (Chaptal, 1804) cit. in (Nencki, 1984); (Leuchs, 1857b)) have been optimised in recent research projects for contemporary use (Hill, 1993; Wurl et al., 1999; Stoker et al., 1998; Garcia-Macias and John, 2004).

Besides the well-explored techniques of woad balls, couched woad and woad pigment, there are also methods documented in literature that seem to be earlier or intermediate forms:

The method documented in the *Papyrus Graecus Holmiensis*, a Greek text from the 3rd century AC (translated and annotated by Lagercrantz (1913) and Reinking (1925)), and the similar method from Corfu (documented without giving a time period or source by Leuchs (1857a)) both describe the processing of woad leaves to a fermented pulp that is dried and used for vat dyeing. The process is similar to the fermenting of leaf pulp in some medieval descriptions, but without forming woad balls and without the subsequent couching process (Table 1, column B). We know from the medieval techniques, that the process of indigotin formation is already completed at the stage of the woad balls (Ewerdtwalbesloh and Meyer, 1998; Kokubun et al., 1998). The

¹ There are techniques documented at the end of the 20th century (e.g. (Hill, 1993; and Grierson, 1989)) that use fresh leaves, however they do not work with indoxyle, but with reduced indigotin: first indigotin is produced from the fresh leaves as for pigment production. Instead of letting the pigment settle and filtering off the liquid, indigotin is immediately reduced again in the same liquid to leuco-indigotin by adding hydrosulphite. The textile is then dyed in this liquid.

² As the terminology around indigo is quite confusing, we provide definitions of how we use the terms in this paper in Appendix A.

Table 1

Classification of woad dyeing methods according to the processing of the dye material.

PROCESSING STEPS	CLASSIFICATION OF DYEING METHODS			
	increasing processing level and concentration of indigotin in the dye material			
	(A) Dyeing with fresh leaves (analogous to methods using <i>Indigofera</i> spp., <i>Strobilanthes</i> spp., <i>Marsdenia tinctoria</i> R.Br., <i>Polygonum tinctorium</i> Ait.)	(B) Dyeing with dried fermented woad leaf pulp (<i>Papyrus Graecus Holmiensis</i> and a recipe from Corfu)	(C) Dyeing with couched woad (medieval woad vat)	(D) Dyeing with woad pigment (vats analogous to vats with indigo from <i>Indigofera</i> spp.)
Step (1) Processing of fresh leaves	Optional: shredding or pounding of leaves (Cardon, 2007; Bühler, 1950)	Pounding of leaves (Leuchs, 1857a; Lagercrantz, 1913; Reinking, 1925)	Optional: washing of leaves (Leuchs, 1857a; Schweppe, 1993; Müllerott, 1991, 1993) Optional: wilting of leaves (Leuchs, 1857a; Edmonds, 1993; Schweppe, 1993; Müllerott, 1991, 1993) Crushing leaves to a pulp (Cardon, 2007; Leuchs, 1857a; Edmonds, 1993, 1998b; Schweppe, 1993; Müllerott, 1991, 1993; Hurry, 1930; Wills, 1979) Optional: fermenting of crushed leaf pulp in heaps for 1 day to 4 months, according to different practices in different countries (Leuchs, 1857a; Schweppe, 1993)	Washing of leaves (Chaptal, 1804)
Step (2) Fermenting of leaf pulp	⚡ Continue step 5	<i>Papyrus Graecus Holmiensis</i> : Leaving pounded leaves in the shade for one day, next day aerating by moving them to achieve equal drying (Lagercrantz, 1913; Reinking, 1925) Recipe from Corfu: Drying pounded leaves in the sun (Leuchs, 1857a)	⚡ Continue step 5	⚡ Continue step 5
Step (3) Forming of woad balls	⚡ Continue step 5	⚡ Continue step 7	Forming of (fermented) leaf pulp into balls, drying of woad balls (Cardon, 2007; Leuchs, 1857a; Edmonds, 1993, 1998b; Schweppe, 1993; Müllerott, 1991, 1993; Hurry, 1930; Wills, 1979) The dried woad balls are also called “green woad” (Cardon, 2007; Hurry, 1930)	⚡ Continue step 5
Step (4) Couching	⚡ Continue step 5	⚡ Continue step 7	Crushing of dried woad balls to a powder, putting into heaps and sprinkling with water. Repeated sprinkling with water and turning the heaps to control humidity and temperature during the fermentation process lasting several weeks (Cardon, 2007; Leuchs, 1857a; Edmonds, 1993, 1998b; Schweppe, 1993; Müllerott, 1991, 1993; Hurry, 1930; Wills, 1979) Optional: sprinkling heaps with urine as well (Müllerott, 1991, 1993) After fermentation: drying and packing of couched woad (Cardon, 2007; Leuchs, 1857a; Edmonds, 1993, 1998b; Müllerott, 1991, 1993; Hurry, 1930; Wills, 1979)	⚡ Continue step 5
Step (5) Macerating of leaves	Macerating the fresh, whole, shredded or pounded leaves in (hot) water, adding alkali (e.g. lime, wood ash lye, and sodium carbonate) (Cardon, 2007; Bühler, 1950) or: macerating leaves directly in wood ash lye or urine (Bühler, 1950; Leuchs, 1857a)	⚡ Continue step 7	⚡ Continue step 7	Macerating leaves in warm water (15–19 °C), ambient temperature > 15 °C enables fermentation (peak of fermentation: after 18–20 h in summer, colour of liquid changes to yellowish green, bubbles) (Chaptal, 1804; Leuchs, 1857b) or: extracting from fresh leaves with hot water, for details see (Leuchs, 1857b) filtering off liquid, adding alkali (limewater), liquid turns cloudy and dark green, flocculates (Chaptal, 1804; Leuchs, 1857b) Stirring and beating the liquid for 15 min–2 h, blue foam appears, waiting for pigment to settle (Chaptal, 1804; Leuchs, 1857b) or (method without aerating): waiting for green sediment to settle, draining off liquid, adding dilute sulphuric acid until it tastes like vinegar, stirring, diluting with water. Waiting for sediment to settle down, draining off liquid (green sediment turns blue without acid as well, but acid cleans indigo of lime) (Chaptal, 1804; Leuchs, 1857b) Draining off liquid, filtering the pigment sludge, drying pigment (Chaptal, 1804; Leuchs, 1857b)
Step (6) Producing of indigo pigment	⚡ Continue step 7	⚡ Continue step 7	⚡ Continue step 7	⚡ Continue step 7

(continued on next page)

Table 1 (continued)

PROCESSING STEPS ↓	CLASSIFICATION OF DYEING METHODS			
	increasing processing level and concentration of indigotin in the dye material →			
	(A) Dyeing with fresh leaves (analogous to methods using <i>Indigofera</i> spp., <i>Strobilanthes</i> spp., <i>Marsdenia tinctoria</i> R.Br., <i>Polygonum tinctorium</i> Ait.)	(B) Dyeing with dried fermented woad leaf pulp (<i>Papyrus Graecus Holmiensis</i> and a recipe from Corfu)	(C) Dyeing with couched woad (medieval woad vat)	(D) Dyeing with woad pigment (vats analogous to vats with indigo from <i>Indigofera</i> spp.)
Step (7) Dyeing	Immersing textile material in the solution for 1–12 h, taking it out and exposing it to air (Leuchs, 1857a; Bühler, 1950; Cardon, 2007) Repeating for darker shades (Bühler, 1950; Leuchs, 1857a)	<i>Papyrus Graecus Holmiensis</i> : Warming woad and urine in a vat in the sun. Next day: mixing it; repeating for 3 days. Boiling the mixture, carefully stirring. Taking off the heat and cooling cauldron from below by pouring cold water on it. Adding soapwort, covering vat and keeping warm on moderate fire for 3 days. Dyeing wool in the vat. The vat can be used twice a day (morning and evening) as long as it works (Lagercrantz, 1913; Reinking, 1925) [The papyrus also describes the process of boiling wool with soapwort and urine, and over dyeing with orchil, which is omitted here] Recipe from Corfu: Pouring water over the dried leaf pulp, when it ferments adding water again and weak wood ash lye, dyeing textile for 8 days (Leuchs, 1857a)	Preparing the vat: Grounding of couched woad, putting it in a vat, adding very hot water and maintaining at 50 °C. Adding alkali (pot ash, urine, lime) until pH 9 (Cardon, 2007) or pH 8.5–9 (Edmonds, 1993; Edmonds, 1998b), stirring. Repeated carefully stirring and controlling pH and temperature until liquid turns yellowish green with a coppery film on the surface ("flower"). This process can take 20–37 h (Cardon, 2007; Edmonds, 1993, 1998b; Schweppe, 1993) Optional: addition of madder, bran, beer, yeast to enforce fermentation (Edmonds, 1993; Schweppe, 1993) Dyeing: Skimming off flower, immersing material in the vat, stirring as little as possible to avoid introduction of oxygen, dyeing for 20 min–2 h according to state of the vat. Taking out, wringing material, exposing to air. Repeating for darker shades (Cardon, 2007; Edmonds, 1993, 1998b; Schweppe, 1993)	URINE VAT: Preparing putrid urine: Keeping urine warm in the sun or close to an oven for 3–4 days up to 3 weeks, then filtering off (Cardon, 2007; Grierson, 1989; Nencki, 1984; Spränger, 1975; Fischer, 1999; Melvin, 2007; Bielenstein, 1935) or: using just urine (Liles, 1999; Bielenstein, 1935) Preparing the vat: Adding indigo in lump or powdered form (put in a muslin bag, suspended in the vat and rubbed daily), keeping the vat warm for 2–4 days up to 4 weeks until liquid turns yellowish–greenish with a coppery film on the surface (Cardon, 2007; Grierson, 1989; Nencki, 1984; Liles, 1999; Spränger, 1975; Fischer, 1999; Melvin, 2007; Bielenstein, 1935). Information about temperature: 30–40 °C (Cardon, 2007; Nencki, 1984; Spränger, 1975), "warm" (Grierson, 1989; Liles, 1999; Fischer, 1999) Optional: stirring the vat daily (Fischer, 1999) Optional: adding dates (Fischer, 1999) Dyeing: Immersing textile for 30 min (Cardon, 2007) or 1–2 days (Grierson, 1989; Nencki, 1984; Liles, 1999; Spränger, 1975; Fischer, 1999; Melvin, 2007; Bielenstein, 1935), exposing to air, repeating for darker shades for up to several weeks, washing and rinsing carefully (Cardon, 2007; Grierson, 1989; Nencki, 1984; Liles, 1999; Spränger, 1975; Fischer, 1999; Melvin, 2007; Bielenstein, 1935) POTASH-MADDER-BRAN-VAT: Preparing the vat: Mixing madder and bran in hot water and keeping at 80 °C for 3–4 h, adding potash and cooling to 40 °C, adding indigo. Keeping vat warm, stirring twice a day (Liles, 1999) Or: mixing madder, bran, wood ash lye or potash in warm water, adding indigo in a tight-weave bag rubbed daily, keeping vat warm for several days up to several weeks, adding additional madder after 2–3 days (Spränger, 1975) Or: boiling of wood ash lye (pH 10) with madder and bran for 15 min., cooling to 40 °C, adding indigo, maintaining temperature, stirring daily and checking pH, adjusting with washing soda to pH 8–9 (Melvin, 2007) Dyeing: When colour of liquid gets yellowish green with coppery flower on the surface, vat is ready for dyeing: immersing textile for 0.5–2 h, exposing to air (Liles, 1999; Spränger, 1975; Melvin, 2007).

Note:

Columns (A) to (D): The methods are classified according to the processing level of the dyeing material. The concentration of indigotin in the dyeing material increases from column A (use of unprocessed fresh leaves) to column D (use of extracted pigment).

Rows: The processing steps are given in rows. All possible steps are listed in the first column on the left. How the steps are applied is described in detail in columns A to D. Additional processing steps that are only mentioned by some authors are indicated as "optional", alternative steps are indicated with "or". The descriptions focus on the process. For quantities – where available – see references quoted.

⚡ Steps that are not applied are indicated with arrows pointing down to the next applied step.



Fig. 2. Woad plot at the University of Natural Resources and Life Sciences Vienna. Picture: © A. Hartl.

subsequent process of couching reduces the plant material (Cardon, 2007) and probably improves the performance of the material in the vat (Kokubun et al., 1998). It is possible that the dried fermented woad leaf pulp described in the Papyrus and in the method from Corfu is similar to the dried woad balls. Dyeing with dried woad balls (“green woad”), without the subsequent couching process, is also historically documented (Leuchs, 1857a), and was tested in our experiments. The fermented leaf pulp mentioned in the Papyrus and in the method from Corfu, however, must be a less concentrated form of the dye than the woad balls because, as Kokubun et al. have established, indigotin formation still continues in the inner parts of the balls until they are completely dry (Kokubun et al., 1998).

2.3. Dyeing with fermentation vats

In traditional vat dyeing techniques, alkaline conditions are established by adding putrid urine, lime or potash for example. The indigotin is reduced by bacterial fermentation, often enhanced by adding madder, sugary fruits, treacle, bran, etc. (Cardon, 2007; Leuchs, 1857a; Grierson, 1989; Nencki, 1984; Liles, 1999; Fischer, 2006; Spränger, 1975; Balfour-Paul, 2006). In “modern” methods developed from the 18th century onwards, the indigotin is reduced by chemical reactions that are quicker and more easily controllable, e.g. the orpiment, copperas,³ zinc or hydrosulphite vat (Cardon, 2007; Leuchs, 1857a; Balfour-Paul, 2006; Blackburn et al., 2009). The hydrosulphite vat is today’s industry standard of vat dyeing with synthetic indigo (Blackburn et al., 2009). Fermentation vats are still used in small-scale artisanal and traditional dyeing in Asia, South America and Africa (Cardon, 2007; Balfour-Paul, 2006; UNESCO and CCI, 2007a, 2007b; ISEND Committee, 2008; Cardon and de la Sayette, 2011). Explanations of the chemical background of the vat dyeing process can be found in literature, e.g. (Cardon, 2007; Schweppe, 1993).

In our experiments, we tested the medieval woad vat with couched woad (Table 1, column C). Representative of the many possible fermentation vat techniques with woad pigment or indigo from *Indigofera* spp., the urine vat (a technique typical for domestic dyeing using human

urine) and the potash–madder–bran vat were chosen for the overview in Table 1 (column D) and the experiments.

When indigo from *Indigofera* spp. was introduced to Europe, woad lost its significance, but was still used in small quantities as a fermentation agent in indigo vats until the end of the 19th century and in Britain even up to the 1930s for dyeing uniforms for the British army and navy (Cardon, 2007). We did not test this method in our experiments since this was not used in prehistoric times due to the absence of indigo.

3. Methods

3.1. Woad processing and dyeing experiments

The development of the processing and dyeing methods was an iterative process, learning from mistakes, consulting (practical) experts and continually consulting literature.

3.1.1. Cultivation and processing

Woad seedlings were planted over 100 m² in April 2010. As woad grows again quickly after cutting, two harvests – the first in July 2010 and the second in August 2010 – were used for the experiments (Fig. 2). The leaves were cut using scissors and washed in water to remove any attached soil. Dyeing with fresh leaves and further processing followed immediately afterwards.

3.1.1.1. Woad balls. The washed leaves were wilted on blankets outside for 1.5–2.5 h and pounded with wooden posts in a plastic tub to a moist pulp. One part of this pulp was formed into balls immediately (“woad balls made of fresh pulp”). The second part of the pulp was kept fermenting for four days (first harvest) and seven days respectively (second harvest), and then formed into balls (“woad balls made of fermented pulp”). The balls were dried on wooden racks outdoors and covered during rain (Figs. 3, 4). In total, 169 woad balls were produced out of 104 kg fresh leaves (Table 2).

3.1.1.2. Couched woad. The dried woad balls (also called “green woad” (Cardon, 2007)) were smashed with a hammer and sprinkled with water. In medieval times, the process of couching was performed in huge heaps that warmed up like compost heaps. For the small amounts used in our experiments, it was necessary to avoid a loss of temperature

³ synonyms: green vitriol, ferrous sulfate, iron(II)sulfate.



Fig. 3. Processing of woad balls: (a) pounding leaves, (b) forming woad balls, and (c) drying in the sun. Pictures: © A. Hartl.

and humidity: the medieval process was simulated in thermos jugs (*KGW Isotherm*), aerated with an air pump of the kind used for fish tanks in a procedure which is applied for compost self-heating experiments (Fig. 5). When the temperature started rising, the material was regularly aerated using a clock timer (aerating for 5 min, every 3 h). The temperature was measured every 10 min with a temperature sensor (*testo 177-T4*). When the temperature dropped, the thermos was opened and the material mixed and, if necessary, also sprinkled with water. When the temperature stopped rising, the couched woad was dried (Table 3, Figs. 6, 7).

3.1.1.3. Woad pigment. Pre-experiments with small amounts of leaves, testing different soaking times (26 h and 45 h) and pH (pH 8.0/8.5/9.0) did not show clearly which method yielded the most pigment.

Therefore the middle variant of pH and a shorter soaking time (which was easier to manage) were chosen for the experiments. The procedure (Table 4) was performed as follows: washed woad leaves were soaked in warm water in a plastic container. The following day, the liquid had a coppery film and bubbles on the surface. The leaves were taken out and the pH raised by adding potash. Immediately after adding potash, the liquid turned yellow-olive and flocculated. The use of a drilling machine with a stirrer for aerating the liquid produced a yellowish foam on the surface which turned blue due to the oxidised indigo. The following day, after the sediment had settled to the bottom of the container, the liquid was filtered through cotton fabric. After drying, the pigment was scraped off the fabric. The pigment from the first harvest showed a greenish-blue colour. The filtering process was lengthy because the whole quantity of liquid was filtered. For the second harvest, the procedure was improved (Table 4) and resulted in a dark blue pigment (Fig. 8).

3.1.2. Development of dyeing methods

We used white, unbleached machine-spun yarn from Merino sheep wool for the development of the dyeing methods. For the ribbon reproductions, hand-spun yarn from the wool of two rare Austrian sheep breeds was dyed.

The wool was washed with a decoction of soapwort (*Saponaria officinalis* L.) to remove wool grease. The yarns were soaked in water before dyeing. After dyeing, the samples were rinsed until the water was clear. We used untreated Viennese tap water (classified as “low to moderately hard”, 6–11°dH⁴) for all the experiments.

The experiment series were numbered chronologically: W1 and W2 for dyeing with fresh woad leaves; V1, V2, etc. for vat dyeing. Each series consisted of several dye baths. In total, 93 dye baths were prepared (32 with fresh woad leaves, 23 with green and couched woad, and 38 with woad pigment and indigo). In most cases, several dyeings were performed in a dye bath. For detailed documentation of all experiments see Appendix B, Tables B.1–B.3.

3.1.2.1. Dyeing with fresh woad leaves. Methods documented for other plants yielding indigoid dyes (Cardon, 2007; Bühler, 1950; Leuchs, 1857a) were adapted. Experiments were performed with leaves from the first harvest to acquire experience (series W1, Table B.1). Dyeings were also carried out in the liquid for woad pigment production (series W0, Table B.1). These experiments were not initially planned, but as the first series with fresh leaves (W1) did not produce satisfactory results, this was also tried because the first steps of pigment production before the aeration of the liquid follow the same principle as dyeing with fresh leaves (see processing steps in Table 1, column A and D). Improved methods with the leaves from the second harvest varied the soaking time of the leaves, the temperature of the soaking water and pH during dyeing (series W2, Table B.1).

The optimal method (W2.2 in Table B.1, Fig. 9) which yielded the best dyeing results – blue colour and even dyeing – and was easiest to manage because of the short soaking times, was chosen for dyeing the hand-spun yarns for the ribbon reproductions:

- (1) 1000 g fresh, washed woad leaves were soaked in a net for 6 h in 4.4 l water (30 °C, incubator). After removing the net with the leaves, the liquid's pH was raised to about pH 8.5 by adding potash.
- (2) For the reproductions, four dippings were performed (0.5 h dipping and 0.5 h aerating each) to achieve darker shades.
- (3) Turning the wool every 10 min during dyeing led to an even colour.

⁴ www.wien.gv.at/wienwasser/qualitaet/haerte.html accessed 17 May 2012 (official website of the Government of Vienna).



Fig. 4. Dried woad balls: (left to right): made from fermented pulp, first harvest; made from fresh pulp, first harvest; made from fermented pulp, second harvest; and made from fresh pulp, second harvest. Pictures: © A. Hartl.

Table 2
Yields of woad balls.

	Woad balls made from fresh pulp		Woad balls from fermented pulp		Total
	1st harvest	2nd harvest	1st harvest	2nd harvest	
Fresh weight of leaves	26 kg	26 kg	26 kg	26 kg	104 kg
Number of woad balls	69	61	39	39	169
Dry weight of woad balls	2855 g	2241 g	2477 g	1812 g	9385 g
Consistency of dry woad balls	Light, not dense, some leaf stalks still visible	Light, not dense, some leaf stalks still visible	Hard and dense, some leaf stalks still visible	Very hard and dense, no leaf stalks visible	

To control the dyeing experiments, we documented the following parameters (verbal description and photo documentation):

- (1) colour change of the liquid due to the addition of potash
- (2) development of a thin skin on the liquid surface
- (3) colour change of the dyed wool during aeration.

3.1.2.2. Dyeing with green woad and couched woad. We conducted five series of vat dyeings with smashed dried woad balls (“green woad”) and couched woad, each consisting of three to six vats (Table B.2). The procedure followed Edmonds (1998b) and Cardon (2007) and was adapted concerning the amount of plant material used,⁵ pH adjustment, frequency of vat process control and dipping duration (Table B.2) to provide an optimal method, eventually yielding a blue colour (V12):

- (1) 70 g of couched woad was mixed with 1.3 l water (80 °C) in a 1.5-litre glass jar fitted with a lid. After cooling to 50 °C and raising the pH with potash, it was kept in the water bath at 50 °C.
- (2) At the beginning, pH 9.0 was adjusted with potash, while during dyeing ca. pH 8.5 proved to be better. During the first days of the experiment, controlling the vat 2–3 times per day and if

necessary adjusting the pH by adding potash was crucial to avoid the pH fluctuating due to fermentation being too great. On the fifth day of the experiment, 0.7 g wheat bran was added to enhance fermentation.

- (3) The first blue dyeing was performed on the fourth day of the experiment, applying four dippings for a dark blue shade (each dipping 2 h and 0.5 h exposure to air for oxidising).

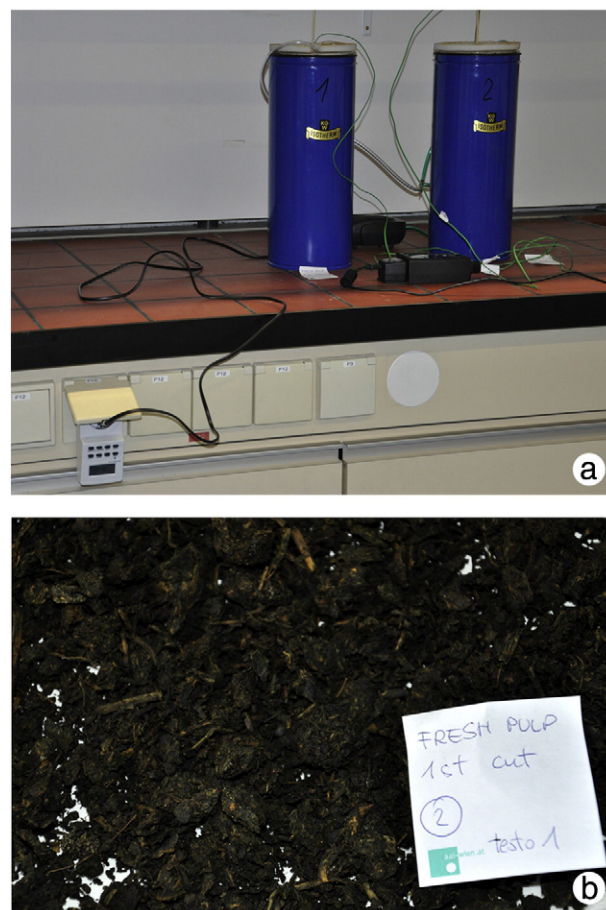


Fig. 5. Woad coupling: (a) thermos jugs with air pump, clock timer and temperature sensor, and (b) couched woad before drying. Pictures: © A. Hartl.

⁵ The amount of couched woad was reduced, because it filled the whole jar leaving no liquid for dyeing. The couched woad used by these authors probably had a different consistency.

Table 3

Woad couching: amounts and pH of the material, duration of the couching process.

	Woad balls made from fresh pulp		Woad balls made from fermented pulp	
	1st harvest	2nd harvest	1st harvest	2nd harvest
Dry weight of woad balls	600 g	600 g	500 g	500 g
Amount of water used for sprinkling crushed woad balls	300 ml	300 ml	200 ml	150 ml
Weight of moistened woad	900 g	900 g	700 g	650 g
Weight of moistened woad used for couching	700 g ^a	800 g ^a	700 g ^b	650 g ^b
Dry weight of couched woad	368 g	423 g	466 g	–
pH of solution of dry woad balls ^c	pH 8.5	–	pH 8.7	pH 9.2
pH of solution of couched woad ^c	pH 9.6	pH 9.5	pH 9.8	–
Duration of the couching process	40 days	40 days	38 days	Experiment stopped after 11 days (no heating up).

Notes:^a Woad balls made from fresh pulp: the volumes of the moistened material from the first and second harvest differed, which is why different amounts were needed to fill the thermos.^b Woad balls made of fermented pulp: the material of the second harvest was harder and less voluminous than that of the first harvest. It would have become too wet if the same amount of water as for the material from the first harvest were used.^c Measuring procedure: 5 g woad was added to 25 g aqua dest., soaked for 30 min, shaken, soaked for 30 min, shaken and measured with pH tester Hanna Instruments HI 98127.

For controlling the vat process, the following steps were crucial:

- (1) observation and photographic documentation of the state of the vat (position of plant material, colour of the liquid in the jar and in glass pipette, bubbles, smell, flower, colour of the wooden sticks used for stirring)
- (2) measuring of pH and if necessary adjusting with potash
- (3) carefully stirring the vat to avoid input of oxygen
- (4) dyeing a test thread before the sample was dyed (Fig. 10)
- (5) documenting the colour change of the dyed textiles due to oxidation.

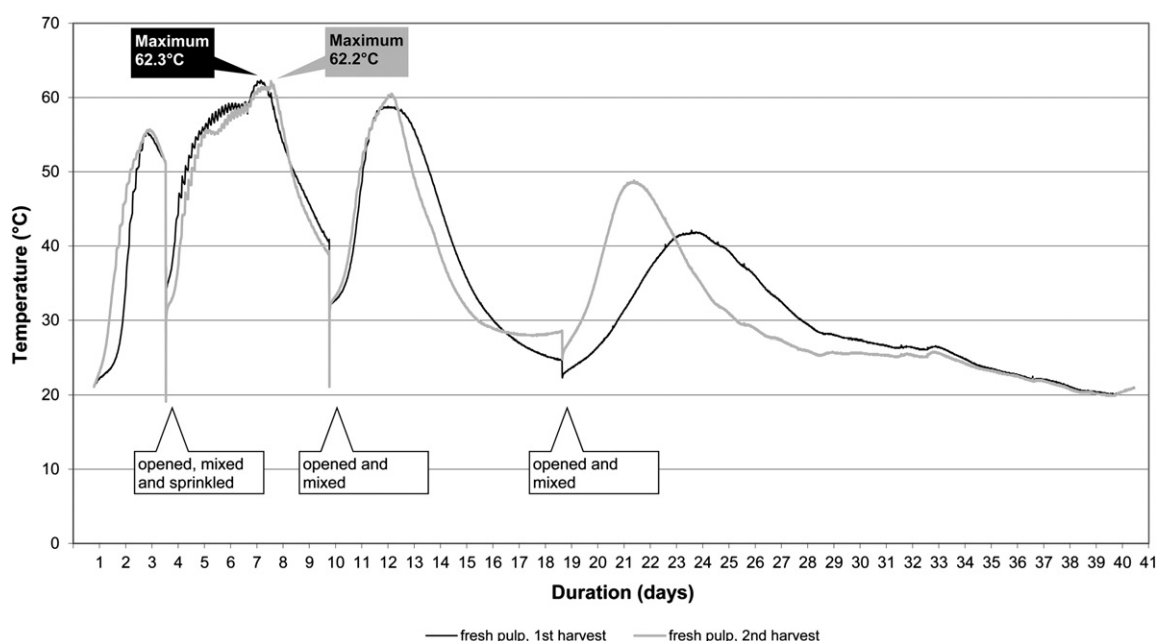
Some dyeings (indicated in Table B.2) were performed with a piece of gauze bandage placed on top of the plant material to avoid contact between the samples and the plant material sludge at the bottom of the jar (Fig. 11).

3.1.2.3. Dyeing with woad pigment and indigo from *Indigofera* spp. To gain experience with these types of vats, the first experiment series were performed with indigo from *Indigofera* spp., using two products available on the market (“indigo Galke” and “indigo Kremer”).

3.1.2.3.1. Experiments with urine vats. The two series consisted of six vats (V1) and two vats (V14). The procedure was based on literature

(Cardon, 2007; Grierson, 1989; Nencki, 1984; Spränger, 1975; Fischer, 1999) and was modified. Human urine was collected and fermented in 1.5-litre jars with a lid at 40 °C in the water bath. The urine was filtered either before the fermentation (series V1) or afterwards (series V14). In series V1, the raising of the pH during urine fermentation took very long or did not work at all, and also problems with mould occurred in some jars. In series V14, where the urine was filtered before fermentation, these problems did not occur. After the urine fermentation, indigo or woad pigment was added and fermented again at 40 °C. The fermentation process was controlled regularly (stirring, measuring pH and documenting visible signs). Dyeings were performed with different dipping durations from 0.5 till 12 h (Table B.3).

Although vat processes using human urine have been successfully performed by others (Fischer, 2006; Fischer, 1999; Melvin, 2007) and are meant to be very easy, it did not work in our experiments. The dyed wool did not show the typical colour change from yellowish–greenish to blue when removed from the vat, which means that the indigo/woad pigment was not reduced properly. In most cases the wool came out of the vat already blue, sometimes it came out greenish–blue or greyish–blue, changing very little to blue. Since the series took 84 and 93 days respectively, the experiments with

**Fig. 6.** Temperature graph of couching woad balls made from fresh pulp.

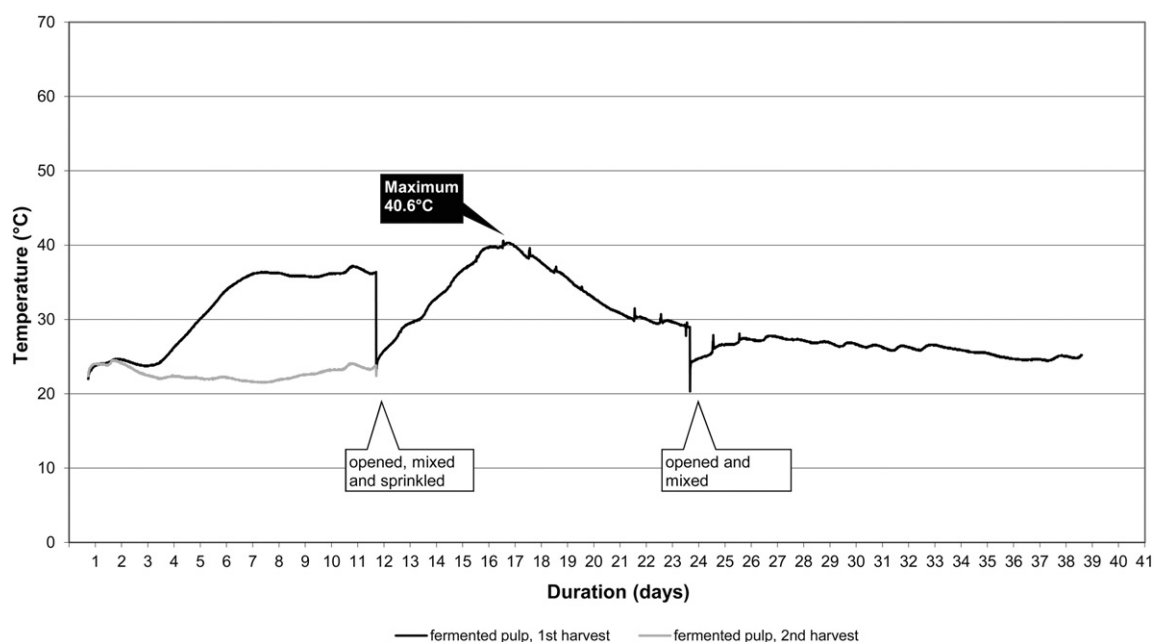


Fig. 7. Temperature graph of couching woad balls made from fermented pulp. The woad balls from the second harvest were very hard and dense, most probably due to the cold and rainy weather during harvesting and the fermenting of the leaf pulp. They did not heat up in the couching process and so the experiment was halted.

Table 4

Woad pigment production.

	1st harvest	2nd harvest Improved method ^a
Fresh weight of leaves	15.5 kg	9.0 kg
Soaking method	Loose leaves	Leaves in nets
Amount of water for soaking leaves	64 l	48 l
Temperature of water poured over leaves	35 °C	18 l water at 60 °C was poured over leaves, then 30 l water at 20 °C was added, the resulting water temperature was 30 °C
Duration of soaking leaves	24 h	20 h
pH after soaking ^b	pH 4.7	pH 4.7
pH after adding potash ^b	pH 8.5	pH 9–10
Amount of potash added	350 g	340 g
Aerating	15 min–30 min rest–15 min	30 min
Duration of pigment settling	16 h	23 h
Filtering through cotton fabric	Filtering whole liquid	Drawing off liquid with a hose and filtering only the bottom sludge
Dry matter of pigment	71 g	35 g
Colour of pigment	Greenish blue	Dark blue

Notes:

^a Improvements after email discussion with David Hill, University of Bristol, UK, 13 August 2010, and also following the procedure described by Stoker et al. (1998).

^b PH measured with Merck pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, special indicator).

urine vats were not continued. Possible reasons for why it did not work could be:

- (1) the temperature of 40 °C during fermentation was too high. Dyers who have experience with urine vats achieved good results keeping the vats close to a heat source such as an oven (about 25–30 °C)⁶ or outside in the garden in the sun (about 20–30 °C).⁷
- (2) The quality of the urine could have been insufficient (however, no medication was taken and eating habits were normal).

3.1.2.3.2. Experiments with potash–madder–bran vats. We conducted eight series of potash–madder–bran vats with indigo and woad pigment, each series consisting of two to six vats (Table B.3). The first series (V2) followed the instructions provided by Spränger (1975). This did not work because the pH was too high and therefore prevented fermentation (pH 11 at the beginning, still pH 9 on the 9th day). The next series (V3) tested an adapted version of Spränger at a lower pH (ca. pH 9–10) and a recipe according to Melvin (2007). Even the adapted version of Spränger did not work (no colour change reaction during dyeing) whereas Melvin's method produced a good dyeing result (intense colour change reaction from yellow/green to blue) and was therefore used for all the following vats. From the next series on, woad pigment was also used, but double the amount than the amount of indigo given in the recipe was necessary. In the first series, the pH at the beginning of the vat process was adjusted to pH 9.5, but a lower pH adjustment (pH 9.0) proved better. After testing different dipping times, a standard duration was used (see below).

⁶ Dorothea Fischer, dyer in Geestacht, Germany, personal communication 09.06.2011.

⁷ Helen Melvin, artist and dyer in Bodfari, Denbigshire, UK, personal communication and experiments conducted with A. Hartl on 28–30.09.2010.

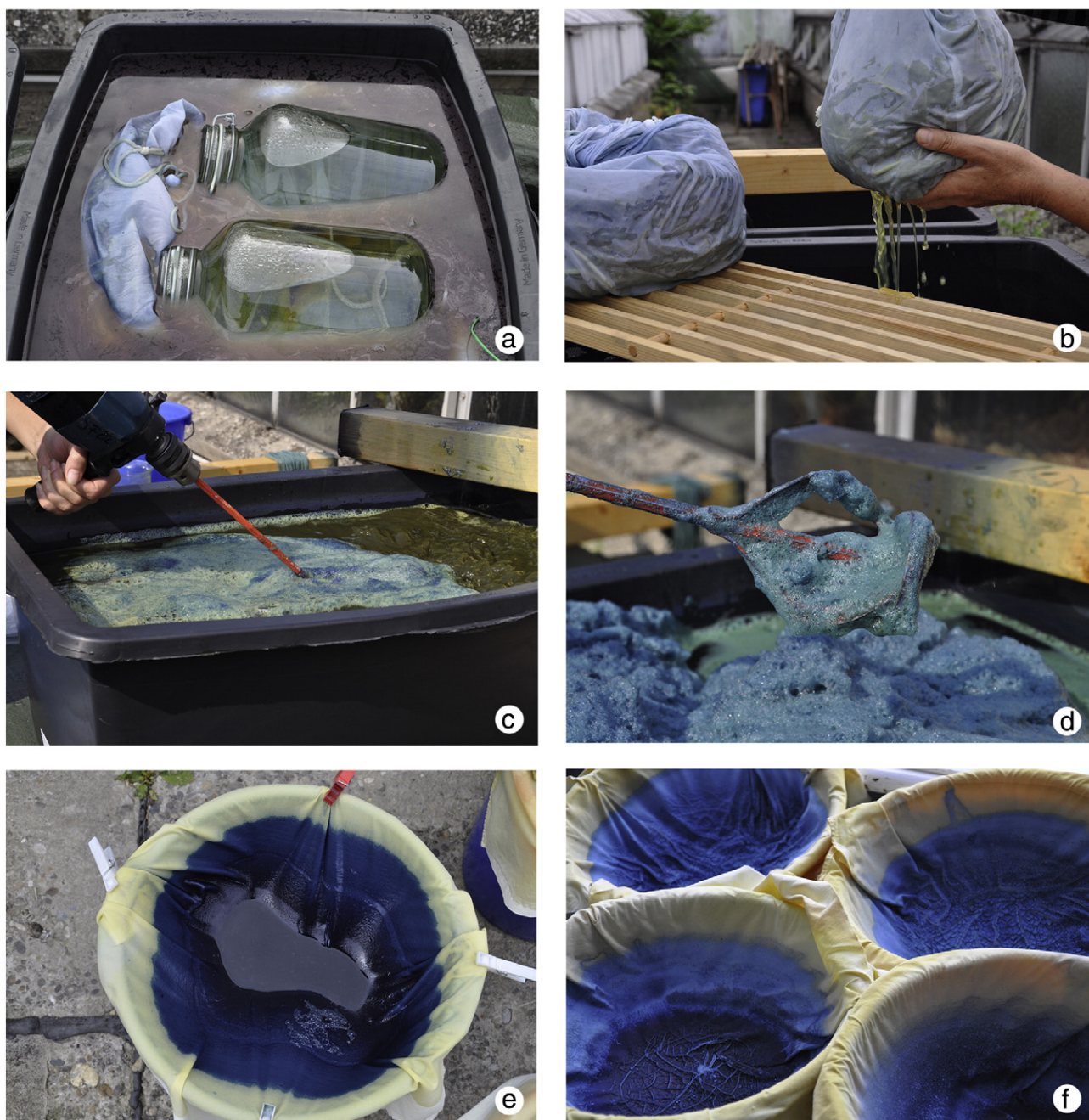


Fig. 8. Producing woad pigment: (a) soaking the leaves in water, (b) removing the nets, (c) aerating the liquid, (d) the foam turning blue due to indigotin, (e) filtering off the pigment sludge, and (f) dried pigment. Pictures: © A. Hartl.

The *optimal method* used for dyeing the hand-spun yarn for the ribbon reproductions (Fig. 12) was as follows:

- (1) 8.7 g madder (*Rubia tinctorum* L.) and 2.9 g wheat bran were mixed with 1.3 l water in a 1.5 litre jar with a lid; pH 9.0 was adjusted with potash and the mixture boiled for 15 min. After cooling to 40 °C, 6.4 g woad pigment was added and the mixture kept in the water bath at 40 °C.
- (2) The pH at the start of the experiment was kept at pH 9.0. As soon as the strong pH fluctuation stopped and the pH only fell slowly, no further pH adjustment was made. The pH remained stable at about pH 8.5.
- (3) The first dyeing was performed on the third day of the experiment. The dipping time was 2 h and 0.5 h exposure to air.

To *control the vat process*, the same parameters as those described in Section 3.1.2.2 were documented.

3.2. Additional mordant dyeing

To compare the analytical results, we performed two reference dyeings with dried woad leaves (sample M4.1) and madder roots (sample 25) respectively. The wool samples were pre-mordanted with alum and dyed according to the procedure described in Table 5.

3.3. Colour documentation and light fastness test

All dyed samples were photographically documented with a colour reference chart. The colours of those samples analysed by HPLC-PDA

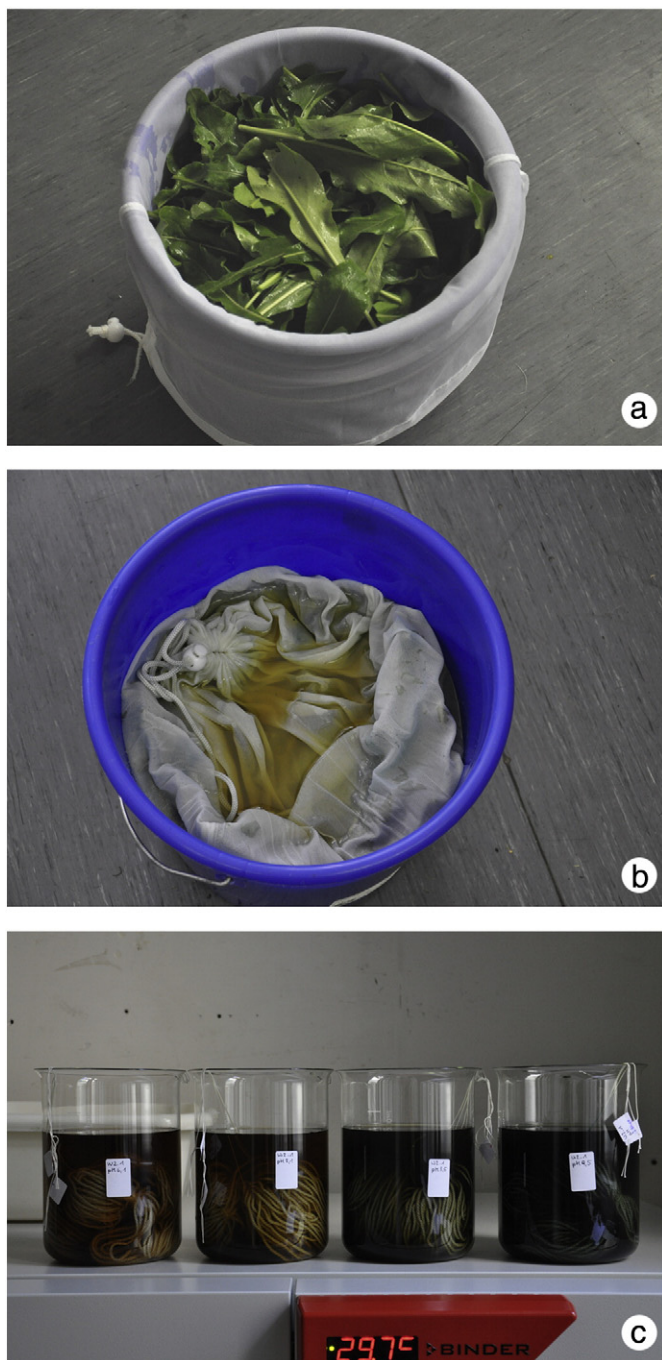


Fig. 9. Dyeing with fresh woad leaves: (a) soaking the leaves in water, (b) colour of the liquid after soaking, (c) dyeing at different pH-values. Pictures: © A. Hartl.

were classified using the Natural Colour System code (www.ncscolour.com/en/ncs) under standardised light (Osram L36W/840, Lumilux Cool White, Hg).

The light fastness of nine samples representing the different woad dyeing techniques and colours was assessed with a Xenon test according to the blue wool standard (ISO 105 B02).

3.4. Dye analysis

In total, 25 dyed wool samples were analysed. The samples represent the blue colours achieved from all the dyeing techniques and the

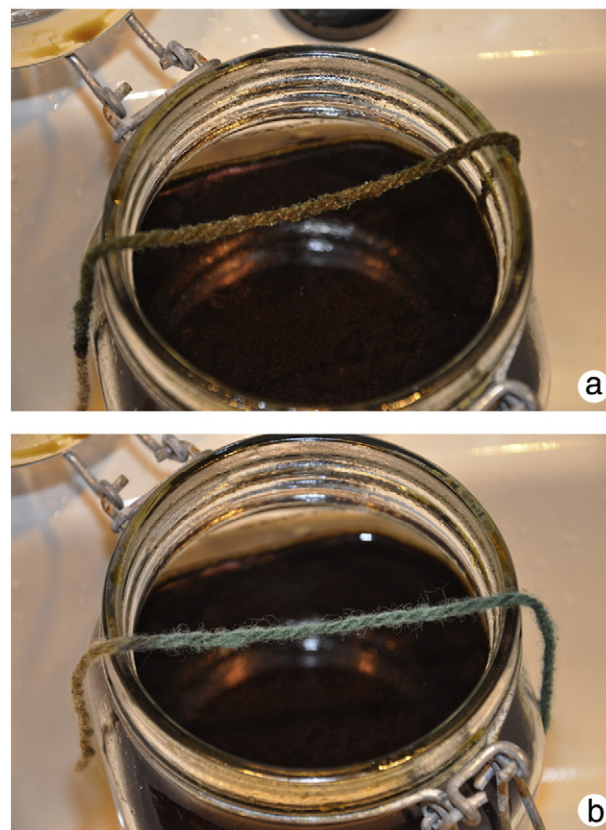


Fig. 10. Dyeing a test thread in a vat with couched woad (V12.2): (a) colour immediately after removing the thread, and (b) colour change after squeezing out the liquid and reaction with oxygen in the air. Pictures: © A. Hartl.

unintended woad colours; additional samples were taken when an explanation for the colours was needed. The dyestuff (woad pigments, indigo, madder used in the madder–bran–potash vats) was also sampled.

The samples were analysed by means of high-performance liquid chromatography coupled with a photo diode array detector (HPLC-PDA). A double-step extraction of the dyed samples was performed in which dimethylformamide (DMF) is first used to extract direct and vat dyes (such as most indigoids), then a hydrochloric acid solution is used to extract mordant dyes. This solvent is evaporated to dryness and the colourants then dissolved using the first DMF fraction. The obtained solution is injected into a column filled with a stationary (solid) phase. Due to differences in adsorption, chromatographic properties and solubility in the liquid mobile phase, the components are separated. Each dye leaves the column at a certain time: retention time (T_r , in minutes).

After separation, the dyes are guided through a photodiode array (PDA) detector which records the ultraviolet–visible absorption spectrum for each individual component. The HPLC-PDA result is usually presented in a chromatogram in which the identified components, based on their PDA spectra, are indicated. The exact analytical procedures are described by Joosten et al. (2006).

4. Results and discussion

4.1. Dyeing blue, and more than blue

It was possible to dye blue with all three dyeing methods after an iterative improvement in the procedures. During this search for blue, however, the colours mint, purple, beige, green and pink were also achieved, as well as various greenish-blue and greyish-blue shades.



Fig. 11. Gauze bandage on top of the plant material. Picture: © A. Hartl.

Contrary to expectations, the light fastness of these untypical woad colours is also fairly good: most of the samples score 6 or 7 on the 8-grade scale (8 being the best value, Table 6).

Only two references in the literature we reviewed clearly mention woad colours other than blue: Plowright (1900), who tested different

Table 5

Mordant dyeing with dried woad leaves (sample M4.1) and madder roots (sample 25) respectively.

	Description of procedure
Preparation of dye bath	The plant material (100% ^a dried and cut woad leaves and 50% ^a madder roots respectively) was soaked overnight in water (dye bath ratio ^b for woad 1:40 and for madder 1:100 respectively), heated up and kept for 1 h at 90° (woad) and 70 °C (madder) respectively. After cooling, the plant material was filtered off and the amount of evaporated water was refilled to maintain the dye bath ratio.
Mordanting	15% ^a alum was dissolved in water (mordant bath ratio ^b for woad 1:40 and for madder 1:100 respectively). The wet wool sample was put in, heated up slowly and kept for 1 h at 90°, occasionally stirred. After cooling down to about 40 °C, the wool was taken out.
Dyeing	The pre-mordanted wool was put into the dye bath, heated up slowly and kept for 1 h at 90° (woad) and 2 hs at 70 °C (madder) respectively, occasionally stirred. After cooling down to about 40 °C, the wool was taken out and rinsed until the water was clear.
Equipment	Beaker glass, magnetic stirrer with electronic contact thermometer

Notes:

^a Percentage refers to the dry weight of the textile material, e.g. if 10 g wool is to be dyed with 100% woad leaves, this means 10 g woad leaves.

^b Ratio of textile material to water, dye bath ratio 1:100 means e.g. for 10 g wool, 1000 ml dye bath was used.

methods for gaining woad pigment, also experimented with dyeing wool with fresh leaves. He describes the colour as “not the dark blue one had expected, but a beautiful pale azure blue.” He noticed: “The blue colour (...) is very subject to variation, being often greenish-blue, grey, or even dove colour.” He gives some detailed recommendations, and ends: “If these precautions be not observed, instead of the indigo-blue, that peculiar brownish-black compound is formed which is the bête noir of the woad experimenter” (p. 331). How true.

Almost 100 years later, Bischof et al. (1998) obtained the following colours with woad, unfortunately without giving any details as to how they achieved them: “pure blue, pure violet, interesting mixture between both (...), a luminous grey (...), brown and red colours that differ from indigotin (blue) and indirubin (violet), yellow, two types of green, that differ much from each other colouristically, black” (p. 33).

The many other colours of woad seem to be an almost unpublished, but nevertheless well-known fact for those who have experimented with woad, as raised in the discussion held after the preliminary results of this research were presented at the DHA30 conference (Hartl et al., 2011). The purple colour achieved with indirubin is also known from dyeing experiments with fresh leaves of dyer's knotweed (*Polygonum tinctorium* Aiton) and *Strobilanthes* sp. (Kohama and Ushida, 2005; Ushida and Kawasaki, 2003).

4.2. Components used for dye analysis data interpretation

Numerous coloured and colourless components were found in the analysed samples (Fig. 13). In all samples, indigotin and indirubin were detected, the predominant components in dyeings with plants containing indigoids, and – in the case of indigotin – responsible for the blue colour. Several components were found with similar PDA spectra to indigotin and indirubin, but eluting at a different retention time. This means that the chemical structure is close to that of indigotin and indirubin, but differs sufficiently to be separated in the HPLC column. These components are labelled indigotin equivalents and indirubin equivalents respectively. Yellow flavonoids which are derived from the woad plant were also detected. In many samples luteolin and a component related to soapwort (*Saponaria officinalis* L.) were found (Appendix C, Fig. C.1), which could both originate from the washing treatment with the soapwort decoction. However, since woad also contains a small amount of luteolin, it could be possible that this originates from woad.



Fig. 12. Hand-spun yarn dyed in a potash-madder-bran vat with woad pigment (V13.2): the yarn turns blue as soon as it is in contact with oxygen in the air. Pictures: © A. Hartl.

Table 6

Colour description and light fastness of samples analysed.

	Samples analysed by HPLC-PDA	Colour description (verbal + Natural Colour System code)	Light fastness ^a	Description of dyeing method
Fresh woad leaves	Sample 1	Mint NCS S 5005-B80G	6	Fresh woad leaves, 1st harvest, 1 dipping for details see Table B.1 , W.0.2
	Sample 2	Purple NCS S 6010-R50B	6	Fresh woad leaves, 1st harvest, 2 dippings for details see Table B.1 , W.0.4
	Sample 3	Light blue NCS S 5020-B	6	Fresh woad leaves, 2nd harvest, 2 dippings for details see Table B.1 , repro
	Sample 4	Blue with purple shade NCS S 5020-R80B	6	Fresh woad leaves, 2nd harvest, 4 dippings for details see Table B.1 , repro
Green woad	Sample 17	Green NCS S 5020-G70Y	6	Green woad, fresh pulp, 2nd harvest, 1 dipping for details see Table B.2 , V6.4
	Sample 26	Beige NCS S 5020-Y	n.a.	Green woad, fermented pulp, 1st harvest, 1 dipping for details see Table B.2 , V6.1
	Sample 27	Beige NCS S 4030-Y10R	n.a.	Green woad, fresh pulp, 1st harvest, 1 dipping for details see Table B.2 , V6.2
	Sample 28	Beige NCS S 6020-B10G	6	Green woad, fermented pulp, 2nd harvest, 1 dipping for details see Table B.2 , V6.3
Couched woad	Sample 5	Blue NCS S 6020-B10G	n.a.	Couched woad, fresh pulp, 1st harvest, 1 dipping (test thread) for details see Table B.2 , V12.2
	Sample 6	Blue NCS S 7020-B	7	Couched woad, fresh pulp, 1st harvest, 4 dippings (white wool dyed together with wool pre-dyed with madder) for details see Table B.2 , V12.2
	Sample 7	Blue, slightly greenish NCS S 6010-B30G	n.a.	Couched woad, fresh pulp, 2nd harvest, 1 dipping (test thread) for details see Table B.2 , V12.3
	Sample 8	Blue NCS S 6020-B	n.a.	Couched woad, fresh pulp, 2nd harvest, 2 dippings (white wool dyed together with wool pre-dyed with madder) for details see Table B.2 , V12.3
Woad pigment and indigo	Sample 9	Blue NCS S 7020-B10G	n.a.	Indigo Galke, potash–madder–bran vat, 5 dippings for details see Table B.3 , V9.1
	Sample 10	Blue NCS S 7020-B10G	n.a.	Woad pigment, 1st harvest, potash–madder–bran vat, 5 dippings for details see Table B.3 , V9.3
	Sample 11	Blue NCS S 7020-B	7	Woad pigment, 2nd harvest, potash–madder–bran vat, 5 dippings for details see Table B.3 , V9.4
	Sample 12	Blue NCS S 5010-B10G	n.a.	Woad pigment, 1st harvest, potash–madder–bran vat, 1 dipping (test thread) for details see Table B.3 , V11.1
	Sample 13	Blue NCS S 5010-B10G	n.a.	Woad pigment, 2nd harvest, potash–madder–bran vat, 1 dipping (test thread) for details see Table B.3 , V11.2
	Sample 14	Blue NCS S 5020-B	n.a.	Indigo Galke, potash–madder–bran vat, 1 dipping (test thread) for details see Table B.3 , V11.3
	Sample 15	Rose NCS S 4030-Y60R	n.a.	“Zero variant”, potash–madder–bran solution, 1 dipping (test thread) for details see Table B.3 , V11.4
	Sample 16	Pink NCS S 5020-R	6	Woad pigment, 2nd harvest, potash–madder–bran vat, 1 dipping for details see Table B.3 , V8.4
	Sample 21	Light blue NCS S 5010-B10G	n.a.	Indigo Galke, potash–madder–bran vat, 1 dipping for details see Table B.3 , V9.1
	Sample 22	Light blue NCS S 5010-B10G	n.a.	Woad pigment, 1st harvest, potash–madder–bran vat, 1 dipping for details see Table B.3 , V9.3
	Sample 23	Light blue NCS S 6010-B10G	n.a.	Woad pigment, 2nd harvest, potash–madder–bran vat, 1 dipping for details see Table B.3 , V9.4
	Sample 25	Red NCS S 2570-Y50R	n.a.	Mordant dyeing with madder + alum for details see Table 5
Mordant dyeings	Sample M4.1	Yellowish NCS S 3040-Y20R	n.a.	Mordant dyeing with dried woad leaves + alum for details see Table 5
	Sample M4.1	White NCS S 0510-Y	n.a.	Not dyed

Notes:

n.a. = not analysed.

Sample numbers not mentioned above are material samples:

Sample 18: woad pigment, 1st harvest.

Sample 19: woad pigment, 2nd harvest.

Sample 20: indigo Galke.

Sample 24: madder roots, used in madder–bran–vats, zero variant and madder mordant dyeing.

^a Light fastness levels according to Blue Wool Standard ISO 105 B02, scale from 1 (worst value) to 8 (best value).

Several coloured components were used for the interpretation of the data: the blue component indigotin, the reddish component indirubin, an unknown red component labelled W495 because its maximum visual absorbance is found to be around 495 nanometers (nm), some unknown light cyan components labelled W597 (maximum visual absorbance around 597 nm), and finally some yellowish flavonoids (maximum visual absorbance around 349 nm). The spectra of the most relevant unknown components are given in [Appendix C](#) (Figs. C.2–C.4).

4.3. Colours and their explanation by dye analysis

4.3.1. Colours achieved by dyeing with fresh leaves

Dyeing with fresh leaves resulted in a colour range from pale blue (almost not dyed) to blue, mint and purple ([Fig. 14](#)). The colours became darker after more dippings, but even four dippings (as applied for the reproductions) did not result in as intense a dark blue as was possible with four dippings in vats with couched woad and woad pigment.

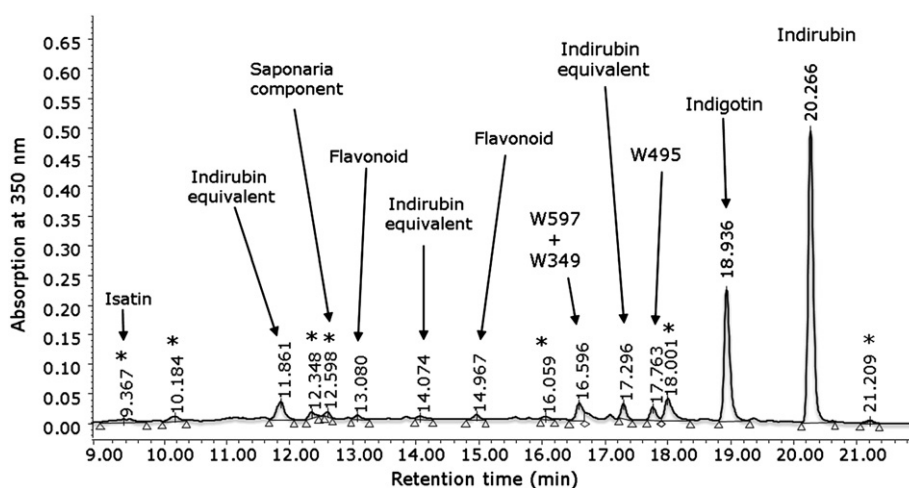


Fig. 13. Typical chromatogram of analysed woad sample. W597 and flavonoid W349 have the same retention time. * indicates colourless components.



Fig. 14. Wool samples dyed with fresh woad leaves from the second harvest. The samples analysed with HPLC-PDA are indicated by the sample number. Picture: © S. Wahlhütter, layout: A. Hartl.

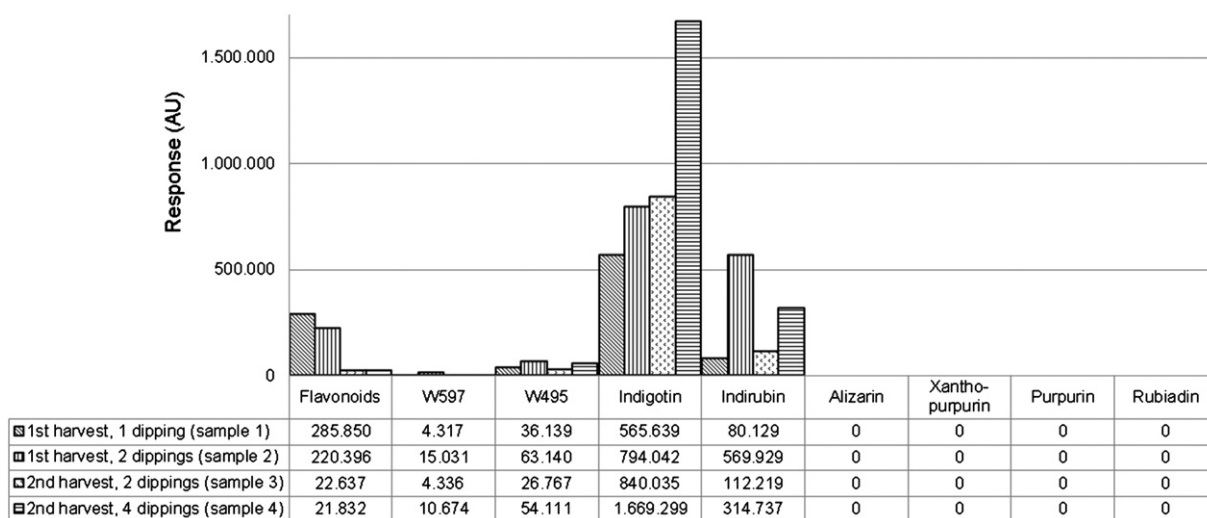


Fig. 15. Analysis results of samples dyed with fresh woad leaves. Response (AU) in the y-axis means absorbance unit.

The dye analysis (Fig. 15) shows that flavonoids and indigotin are the main components in sample 1 (mint). The concentration and ratio explain the colour observed. However, when organic colourants are present in low concentrations, as is the case in this sample, the ecru colour of the unbleached wool may also play a role in the visual perception. Concerning the dyeing procedure, the reasons for this singular occurring mint colour remain unclear. In sample 2 (purple), indirubin and indigotin are present in almost equal concentrations, which explains the purplish colour. Purple colours (see also series W2.6 in Fig. 14) seem to occur at higher temperature of the soaking water and longer soaking duration (Table B.1). In sample 3 (light blue), indigotin predominates, but its concentration is low and results in a soft blue hue. In sample 4 (blue with purplish shade), the concentration of indigotin is higher, and so is the hue saturation. A purplish shade was also observed in this sample, which may be due to the relatively high amount of indirubin and component W495.

4.3.2. Colours achieved by dyeing with green and couched woad

Dyeing with green woad balls and couched woad resulted in beige, green and bluish green colours (Fig. 16). With couched woad, it was possible to dye a dark and intense blue as well after gaining experience and improving the methods (Section 3.1.2.2 and Table B.2). With green woad balls, we did not manage to dye the wool samples blue, however the gauze bandage pieces which were placed in some vats on top of the plant material during dyeing showed intense blue shades. Evidently the fibre material of the gauze bandage had a greater affinity to the dyes than the wool yarns used.

The typical green colour (sample 17) can be explained by dye analysis as a mixture of blue and yellow dyes: next to indigotin, flavonoids are present in high concentrations. Flavonoids are normally known as mordant dyes, i.e. they require a mordant (metal salts such as aluminium, iron or copper salts) to be permanently fixed to the fibre (Cardon, 2007; Schweppe, 1993). Obviously they also attach to the fibre when no mordant is applied via direct dyeing. In the beige sample 27, not only is the flavonoid ratio higher than in the green sample 17, but the concentration of the light cyan component W597 is also much higher than in the other samples, while that of indigotin is lower (Fig. 17).

The high concentration of flavonoids present in the dyeings with green woad balls was the motivation behind analysing a mordant dyeing with alum and dried woad leaves (sample M4.1). In this sample, the same flavonoids as in the green woad ball dyeings (samples 17 and 27) are present in very high concentrations, hence the yellowish colour. Indigotin is not bound to the textile fibre as no vat dyeing

was performed. It is interesting, however, that the concentration of indirubin detected in sample M4.1 was relatively high (Fig. 17). Kokubun et al. (1998) found indigotin and indirubin in dried woad leaves as well, but much less so than in woad balls.

In the blue dyeings with couched woad (samples 5, 6, 7 and 8, Fig. 18), indigotin predominates in all samples. As with the dyeings with green woad (samples 17 and 27, Fig. 17), those with couched woad also show a higher concentration of the light cyan component W597 than in the samples dyed with fresh leaves (Fig. 15). It is not certain whether the relatively high concentration of this component is typical for dyeings with green and couched woad and requires further experimentation for this to be proven.

Samples 5, 6, 7 and 8 show a similar composition concerning the components W597, W495, indigotin and indirubin. Sample 7 has a more greenish appearance due to the ratio between yellow flavonoids and indigotin.

As green and couched woad still contain a lot of plant material, several other colourants are present in the vat as well, such as flavonoids, W597 and W495. The reason why sometimes more flavonoids were detected on the dyed fibres (and therefore caused the beige or green colours), is probably due to the state of the vat, i.e. the reducing conditions. But also other factors must be involved, otherwise the gauze bandage and the wool yarns which were dyed in the same vat would not show different colours. It also remains unclear why there are less flavonoids detected on the dyed fibre when there is a lot of indigotin: although the flavonoids must be also present in the vat, only a few attach to the fibre.

The low concentration of the madder components xantho-purpurin, alizarin and rubiadin in samples 6 and 8 (Fig. 18) is due to contamination, because other samples pre-dyed with madder were dyed in these vats at the same time (Table B.2 in Appendix B). Samples 5 and 7 were test threads that were dyed before samples 6 and 8, and are therefore not contaminated.

4.3.3. Colours achieved by dyeing with woad pigment

Dyeing with woad pigment in potash-madder-bran vats gave beige, pink, bluish and intense blue colours; the dyeings with indigo show a much smaller variety of shades (Fig. 19).

The predominant components in all blue samples dyed with woad pigment are indigotin and indirubin. In addition, flavonoids, W597, W495 and minor indigoid components such as the indirubin equivalents were all present, but in very low concentrations, much lower than in the dyeing techniques using fresh leaves and green or couched woad. Fig. 20 shows the results for samples 21, 22 and 23 (the results

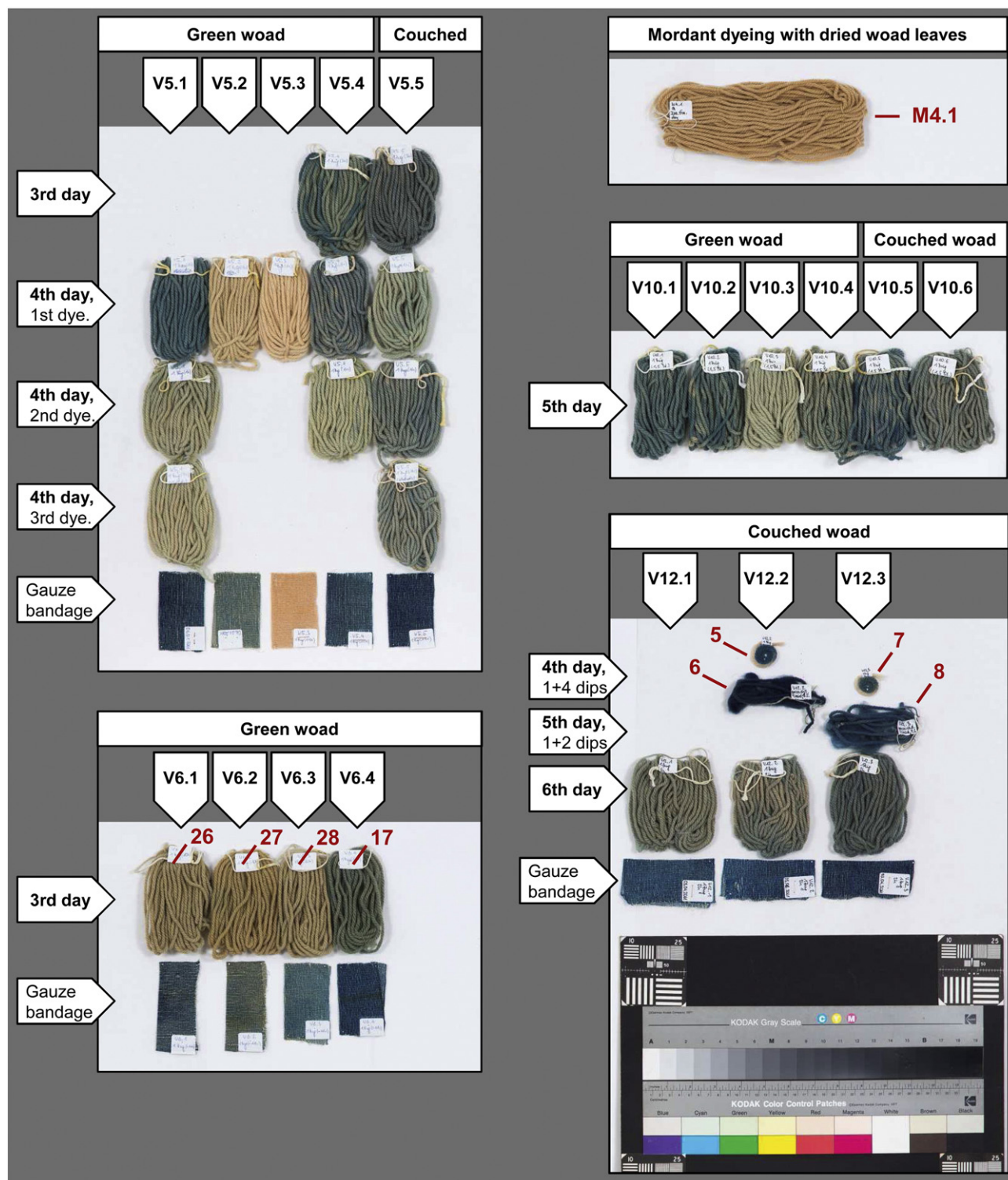


Fig. 16. Samples dyed with green and couched woad. The samples analysed with HPLC-PDA are indicated by the sample number. The picture also shows the dyed pieces of gauze bandage which were placed on top of the plant material in some vats. All samples dyed with one dipping unless otherwise indicated. Picture: © S. Wahlhütter, layout: A. Hartl.

for samples 9, 10, 11, 12, 13 and 14 were more or less the same). Using woad pigments therefore resulted in a 'cleaner' dyeing than using dye-stuff that still contains more plant material. The flavonoids and the components W597 and W495 were not detected in any of the three samples dyed with indigo (samples 9, 14 and 21).

In the samples dyed in potash-madder-bran vats, several anthraquinones such as alizarin, xantho-purpurin and rubiadin were detected, which originate from the madder roots used in the vat preparation.

Interestingly, almost no purpurin was found. The concentration of rubiadin was much higher compared to alizarin, while in mordant dyeings with madder both alizarin and purpurin (or their glycosides) predominate ((Schweppe, 1993; Hofenk de Graaff, 2004); the effect can be seen in sample 25, Fig. 21).

In the blue samples, the anthraquinones do not have any visual effect on the colour of the dyed wool. The pink colour of sample 16 is due to alizarin and rubiadin (Fig. 21). This sample was dyed in V8.4, a series

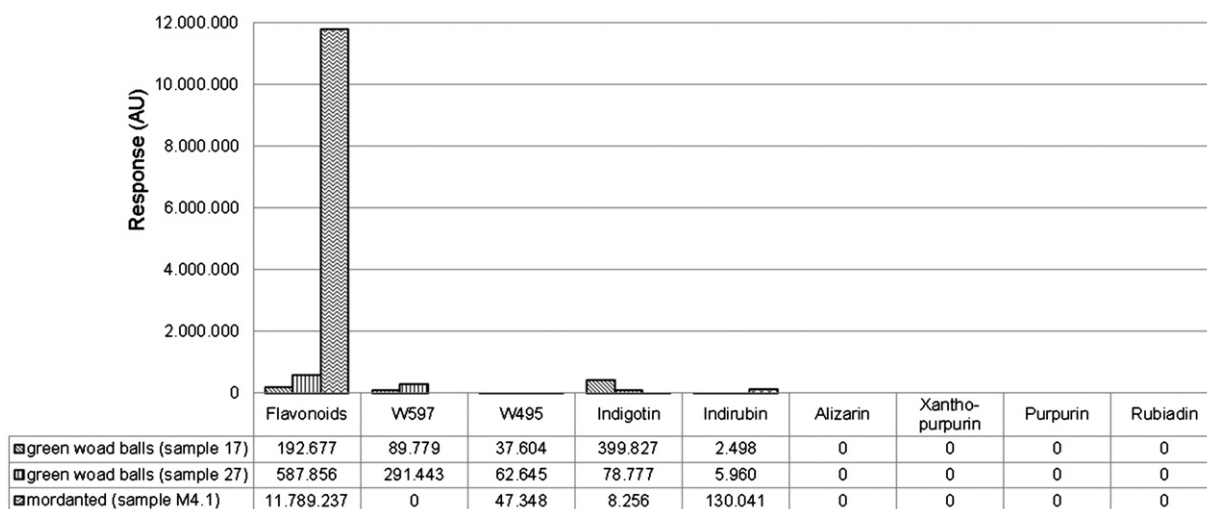


Fig. 17. Analysis results of samples dyed with green woad and one mordanted sample dyed with dried woad leaves.

not yet optimised as regards the amount of woad pigment, and also at a very early stage of the vat experiment where the indigotin was not yet sufficiently reduced, which may be the reasons for the colour. Sample 15, dyed in the “zero variant” which was kept under the same conditions as the vats but without adding woad pigment, also shows a pinkish colour. This is due to the anthraquinones alizarin and rubiadin; compared to samples 12, 13 and 14, the amounts of these anthraquinones are higher, but compared to sample 16 the amounts are more or less the same.

4.4. Comparison of the different dyeing techniques

Indigotin and indirubin were found in all samples dyed with woad, but in different ratios. More important is the presence of other woad-related components that differs in these samples (Fig. 22, results of four samples that are examples of the analysed dyeing techniques).

The samples dyed with couched woad show a much higher amount of flavonoids compared to the other vats. Flavonoids are also present in the samples dyed with fresh leaves and green woad, and are completely absent in the vats with woad pigment. The

flavonoid indicated in Fig. 22 is not the only flavonoid detected; others are also present (summarised as “flavonoids” in Figs. 15, 17, 18, 20 and 21). Different flavonoids were found in samples dyed in different vats. If present in high amounts, the yellow flavonoids induce a greenish shade.

The unknown light cyan component W597 is present in a relatively high amount when green woad and couched woad were used, and at a very low concentration when fresh leaves and woad pigment were used. It appears that this component is created by the fermentation which takes place during the processing of the leaves to woad balls and couched woad.

In the samples dyed with fresh woad leaves, the concentration of the reddish component W495 is higher than the concentration of W597; in all the other samples, however, the concentration of W495 is lower than that of W597. Comparing the different dyeing techniques, the concentration of W495 is more or less the same in all samples, except for the samples dyed with woad pigment, where it is much lower.

In the samples dyed with woad pigment in potash–madder–bran vats, rubiadin was detected, which is a marker for the madder used.

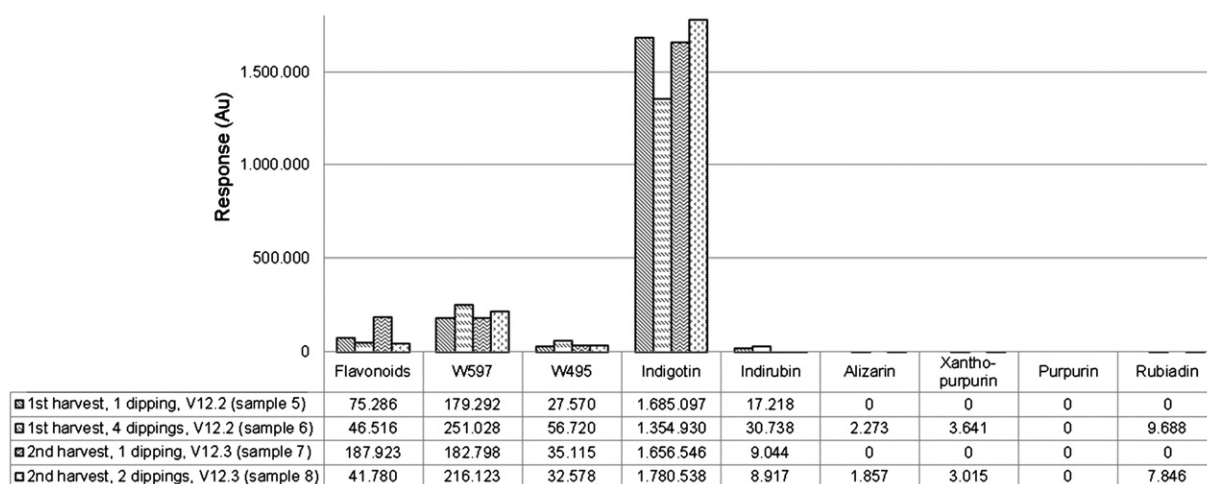


Fig. 18. Analysis results of samples dyed with couched woad. Sample 5 is a test thread dyed in the same vat (V12.2) before sample 6 was dyed. Sample 7 is a test thread dyed in the same vat (V12.3) before sample 8 was dyed. Both samples 6 and 8 were white wool, but were dyed with other samples pre-dyed with madder, which caused the contamination with the madder components xantho-purpurin, alizarin and rubiadin.



Fig. 19. Samples dyed in potash–madder–bran vats with woad pigment and indigo respectively. The samples analysed with HPLC–PDA are indicated by the sample number. All samples dyed with one dipping unless otherwise indicated. Picture: © S. Wahlhütter, layout: A. Hartl.

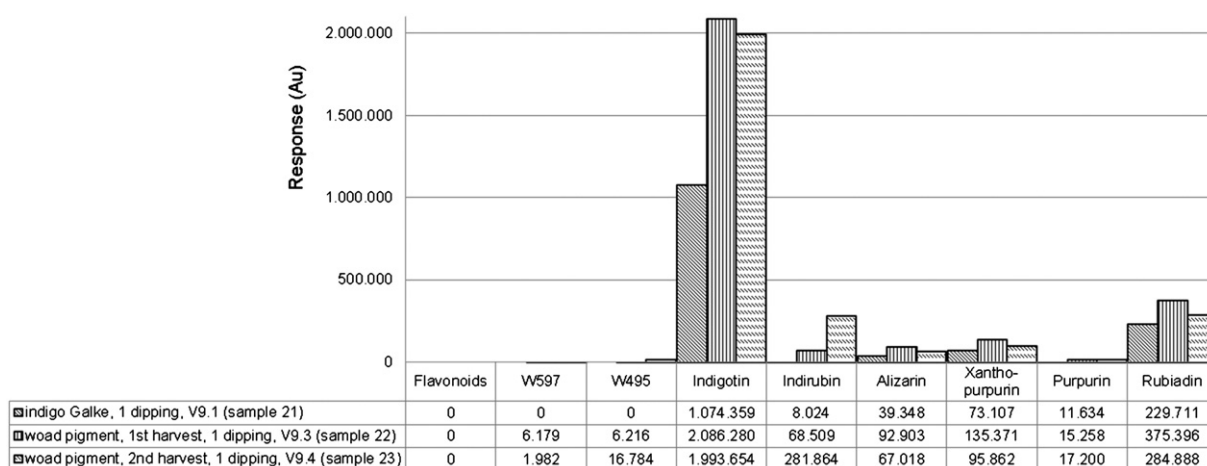


Fig. 20. Analysis results of samples dyed with woad pigment and indigo respectively.

4.5. From analytical results to colour calculation

In general, we were able to explain the colour of the samples based on a qualitative evaluation of the analytical results. However, it is also possible to be more exact and use quantitative information. The UV-vis spectra obtained with PDA detection can be used to calculate RGB values (i.e. red, green and blue), in order to determine whether or not the colour observed corresponds to the components and their concentration detected with HPLC analysis.

The absorption spectrum data of each component is extracted and translated into transmission using a spectral calculator. Since some dyes are halochromic, i.e. absorbance behaviour is affected by pH during the HPLC analysis, pH is regulated with a post-column buffer solution. In addition, calculations are undertaken to compensate for any dilution step in the extraction by considering sample weight, dilution factor and actual injection volume.

Each coloured component with a certain hue differs in intensity depending on the concentration, e.g. indirubin has a dark violet to bright bluish-pink appearance (Fig. 23). Several other minor components can have an effect on colour too if a number of them are present. Since absorption spectra are additive, the colour calculation can be performed using all the dyes present in the chromatogram per sample for a more accurate colour calculation. The calculated colours were visually compared with the colours of the yarns and presented a good match (Fig. 24). This enabled us to show that all the components characterised by HPLC analysis were indeed responsible for the overall colour in these samples.

5. Conclusions

Traditional woad processing and dyeing techniques have been thoroughly explored, as shown by the review of scientific and practical

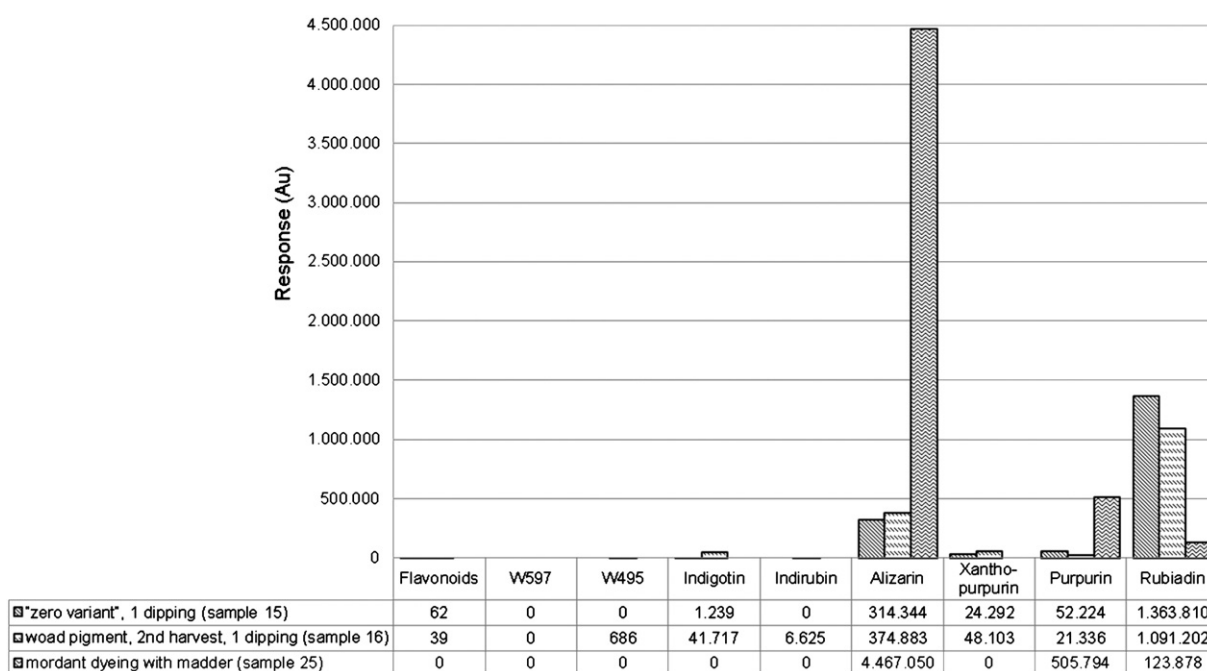


Fig. 21. Analysis results of a sample dyed with woad pigment in comparison to samples dyed with madder (*Rubia tinctorum* L.). The small amount of indigotin in sample 15 could come from cross-contamination, either a post-dyeing, mechanical contamination or a system sample carryover. The peak of 1.239 is just above detection limit.

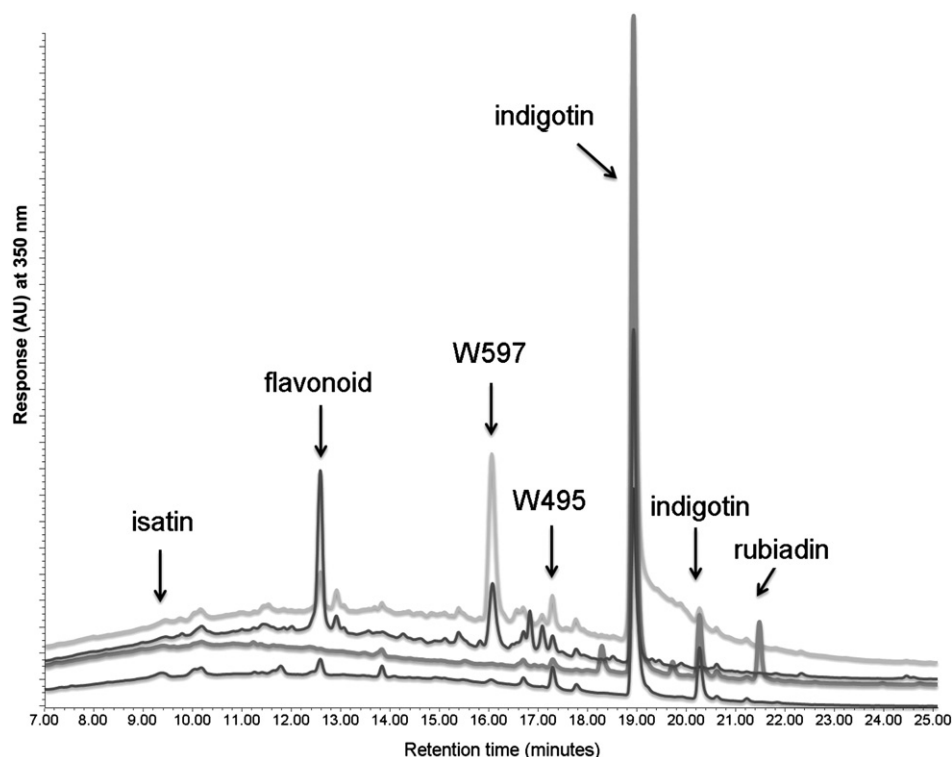


Fig. 22. Qualitative comparison of dyeing techniques. Chromatogram lines from bottom to top: bottom line: fresh woad leaves (sample 3); second line: woad pigment (sample 10); third line: couched woad (sample 7); top line: green woad (sample 17).

literature. Despite the fact that there is a large amount of written documentation, dyeing blue still presents a challenge: methods need to be adapted to the material used; there is sometimes an absence of the necessary details in literature; and – most of all – controlling and managing the vat process requires considerable experience. Cooperating with dyers experienced in fermentation vats was very useful. We succeeded in reconstructing blue colours with methods using fresh leaves, green and couched woad and woad pigment. Still the blue colours could be brighter. Improvements could be made by using bleached, pure white wool and further optimisation of the techniques.

The colour differences of the samples dyed with woad can be explained by the results of the HPLC analysis. The most predominant component in blue woad dyeing is indigotin. When other coloured components present in woad, e.g. flavonoids and indirubin, appear in higher concentrations due to the processing and dyeing technique or due to the state of the vat, other colours can be achieved. Colour calculations from PDA spectra allowed the hues of single or mixed coloured components to be reconstructed and the approximate colour of the sample caused by organic colourants to be defined. It enables an understanding of the colour observed, but can also establish whether other components are present which affect the colour but are not detected by HPLC-PDA analysis. If the calculated colour is different from that observed, a possible inorganic factor has to be taken into account. Colour differences caused by inorganic components (e.g. mordants, metallic contaminants and soot) can be identified with other analytical techniques, e.g. SEM-EDX (scanning electron microscopy with energy-dispersive X-ray analysis). The colour calculation, however, cannot be used to reconstruct the original colours of (pre)historic textiles, as in that case the degradation processes of dyes and fibres should also be taken into account.

With the HPLC-PDA method, it was possible to detect anthraquinones at low concentrations in the samples dyed in madder-bran vats. These red components did not affect the overall colour. Interestingly, the ratio of the anthraquinones differed from that normally found in mordant dyeings with madder, and might therefore indicate the use of this kind of madder-bran-vat.

The samples dyed in dye baths with fresh leaves, green woad and couched woad showed a consistently higher concentration and a larger variety of coloured components derived from woad in contrast to samples dyed with woad pigment or indigo. This can be explained by the amount of components other than indigotin and indirubin being reduced during pigment preparation. Since there were analytical differences between the investigated dyeing techniques, it was easier to distinguish between dyeing techniques when samples were dyed with woad or indigo by looking at the ratio of components present.

The components W495 and W597 occurred in all woad-dyed samples (although in different concentrations), but did not occur in the samples dyed with indigo. If these components are typical for woad, we would also be able to identify whether this plant species was used for dyeing when historic textiles are analysed.

It has to be considered that differences in the processing and dyeing processes formerly used may produce different results, and that practical use of the textiles (repeated washing, exposure to light, etc.) and time may also have an effect on the components detected. Further research is required to apply the findings here to the analysis of (pre)-historical textiles.

Abbreviations

DMF dimethylformamide

HPLC-PDA high-performance liquid chromatography with photo diode array detection

PDA photo diode array detection

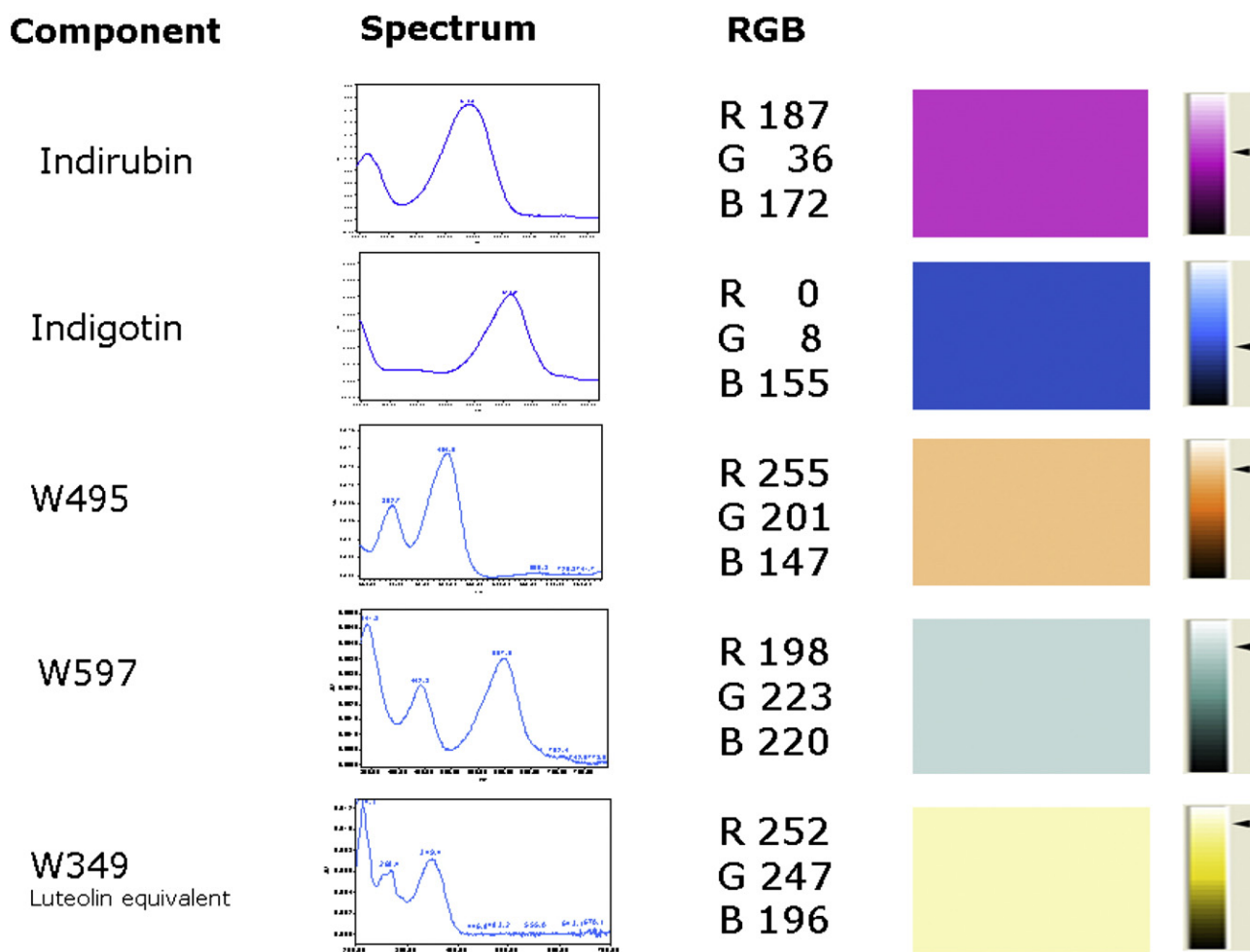


Fig. 23. Spectra of the main woad components and their translation into RGB colours.

RGB red, green, blue
 SEM–EDX scanning electron microscopy with energy-dispersive X-ray analysis
 T_r retention time
 UV–vis ultraviolet–visible

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Appendix A. Definition of terms

Indigo: In everyday but also scientific language, the term “indigo” is applied to the plants, the traded extract, the chemical component indigotin, as well as the blue colour. In this paper, we use it exclusively for the traded product, an extract mostly in the form of a powder or block (“cake”), sometimes also in the form of a paste that contains indigotin and other related components such as indirubin. For indigo gained by chemical synthesis we use the term “synthetic indigo”. To avoid the term “woad indigo”, which is found in literature for the extract gained

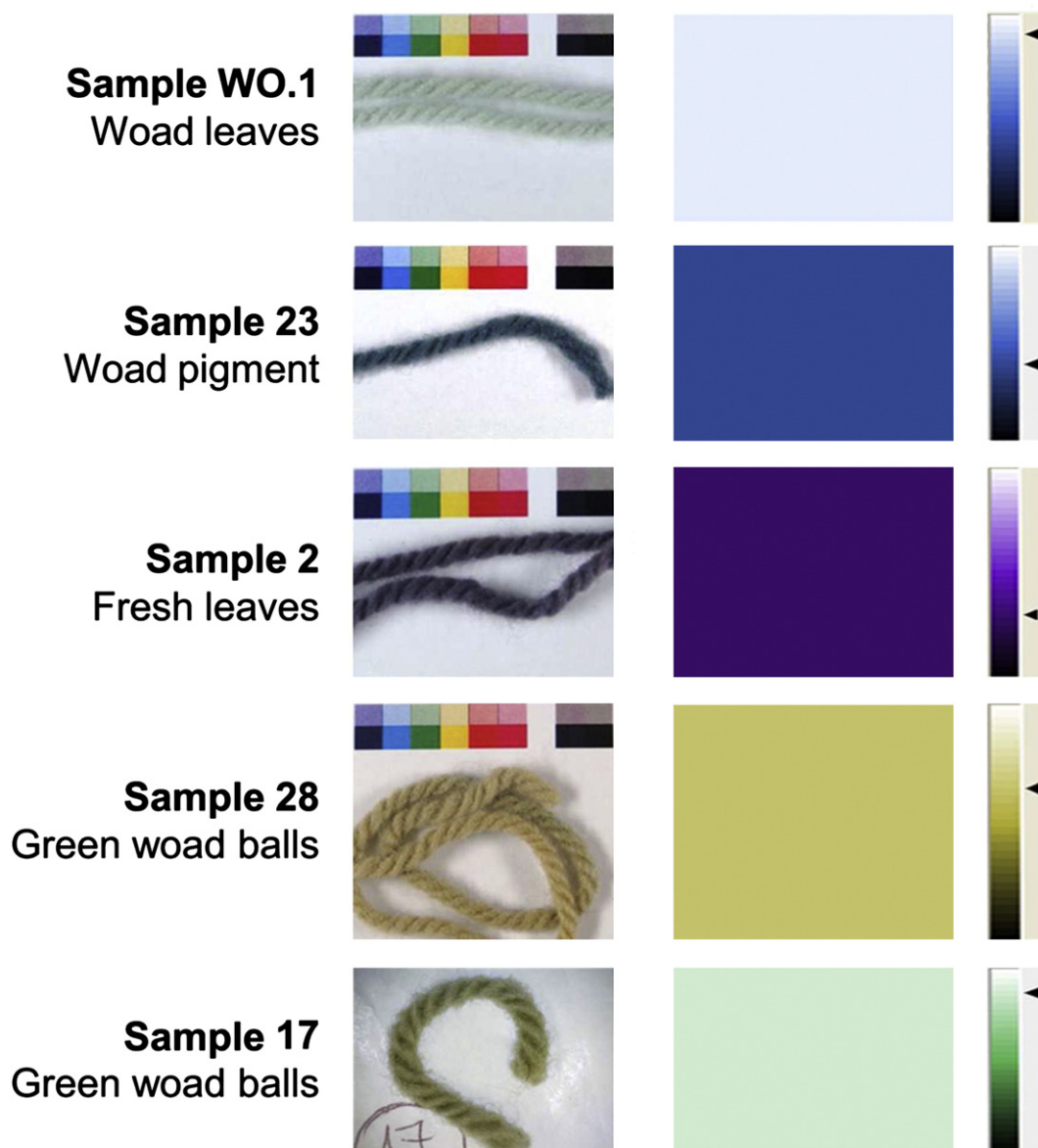


Fig. 24. RGB colour calculation of selected samples. Sample WO.1: the main component is indigotin present in a low concentration. The colour of indigotin predominates, but the concentration is low so the ecru of the wool also has an influence on the colour. Sample 23: the concentration of indigotin is much higher than in sample WO.1, resulting in an intense blue. The other components detected are at such low concentrations that they have no effect. Sample 2: the blue indigotin and the reddish indirubin are present in approximately the same concentrations, resulting in a purple colour. Sample 28: the beige colour is due to yellow flavonoids which predominate in relation to the low concentrations of indigotin and indirubin. Sample 17: indigotin and flavonoids are both present in almost the same concentrations. The RGB-calculated colour differs slightly from the colour of the sample due to many other flavonoids which were not considered in the calculation. Including these components would give a more consistent result.

from fresh woad leaves, we prefer the term “woad pigment”, as used by two European woad processing companies.

Indigotin: We use this term for the main colouring component, a blue pigment, following e.g. Cardon (2007) and Hofenk de Graaff (2004). In other scientific literature, e.g. in the fields of chemistry and textile chemistry, the term indigo is used as a synonym.

Indigoids: This is a generic term used for indigotin and structurally related components (indirubin and the *cis*-forms of indigotin and indirubin), and also including the components of purple (e.g. dibromindigotin). We follow the classification of Schweppe (1993), who under this term also lists the precursors (e.g. indican and isatan), and intermediate and degradation components (e.g. indoxyl and isatin), as well as indigo-carmine, a semi-synthetic dye produced from natural or synthetic indigo and sulphuric acid.

Plants yielding indigoids: The technique of gaining indigo and other preserved forms of the dye has been developed all over the world using

locally available plants of different genera, such as woad (*Isatis tinctoria* L.), dyer's knotweed (*Polygonum tinctorium* Aiton), various *Indigofera* species, Assam indigo (*Strobilanthes cusia* Kuntze), Yoruba indigo (*Philenoptera cyanescens* Roberty) and many more (30 species are documented in detail by Cardon (2007); Bühler (1948) mentions more than 50 species). We summarise these as “plants yielding indigoids”. The main plant species used for the production of indigo traded to Europe are *Indigofera* species. In most cases there is no information about the *Indigofera* species from which the indigo was actually made. The best known species is *Indigofera tinctoria* L. Cardon describes several more which were once particular to specific regions, but were later also cultivated in other tropical countries (Cardon, 2007). Due to the lack of evidence, we only give the Latin name of the genus (*Indigofera* spp.). We avoid the terms “indigo plant” or “indigo plants”, which are found in literature for both the particular species *Indigofera tinctoria* L. as well as for summarising the various plant genera yielding indigoids.

Appendix B. Process of dyeing method development

Table B.1

Dyeing with fresh woad leaves.

Series	Dye baths prepared per series	Preparation per jar	Dyeing	No. dye baths	No. samples
W1 first harvest	W1.1: boiling water, soaking 0.5 h, + potash lye W1.2: boiling water, soaking 1 h, + potash lye W1.5: water 50 °C, soaking for 5.5 h, + potash lye W1.8: potash lye 50 °C, soaking for 7 h at 50 °C W1.10: boiling water, soaking 1 h, + wood ash lye Missing numbers: abandoned variants (the initial research plan was reduced).	W1.1: 2 l of boiling water poured over 0.5 kg woad leaves, soaked for 0.5 h at 50 °C (incubator), then filtered off. 1 l of the liquid was mixed with 0.5 l of potash lye with pH 11, resulting in pH 9.0 of the mixture. W1.2: same as W1.1, but soaking for 1 h, resulting in pH 9.0 of the mixture. W1.5: 2 l of water at 50 °C poured over 0.5 kg woad leaves, soaked for 5.5 h at 50 °C (incubator), then filtered off. 1 l of the liquid was mixed with 0.5 l of potash lye with pH 11, resulting in pH 8.5 of the mixture. W1.8: 2 l of potash lye at 50 °C poured over 0.5 kg woad leaves, soaked for 7 h at 50 °C (incubator), then filtered off. 1 l of the liquid was used for dyeing (pH 9.0). W1.10: 2 l of boiling water poured over 0.5 kg woad leaves, soaked for 1 h at 50 °C (incubator), then filtered off. 1 l of the liquid was mixed with 0.5 l wood ash lye with pH 11.8, resulting in pH 9.0 of the mixture. pH measured with Merck pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, Special indicator)	W1.1, W1.2, W1.10: the yarn samples were put in at the same time and taken out after 0.5 h/1 h/1.5 h/13 h. W1.5: samples taken out after 0.5 h/1 h/1 h + 1 h (2 dippings). W1.8: samples taken out after 0.5 h/1 h/13 h. Dippings for 0.5 h/1 h/1.5 h: at room temperature, dippings for 13 h: at 50 °C in incubator. Sample size: each sample 5 g.	5	18
W2 second harvest	W2.1: soaking 3 min in boiling water, dyeing at 30 °C W2.2: soaking 6 h, water 30 °C W2.3: soaking 12 h, water 30 °C W2.4: soaking 24 h, water 30 °C W2.5 (Hill^a): soaking 24 h, special procedure W2.6 (reproducing violet): soaking 24 h, water 35 °C	W2.1: 1600 g of woad leaves soaked for 3 min in 9 l of boiling water, leaves removed, cooled down quickly by putting in cold water. Liquid divided into 4 dye baths (each 2.2 l) at different pH levels: without adding potash (pH 6.1)/pH 8.1/pH 8.5/pH 9.5. W2.2: 800 g of woad leaves soaked for 6 h in 4.5 l of water (30 °C, incubator), leaves removed. Liquid divided into 4 dye baths (each 1.1 l) at different pH levels: without adding potash (pH 5.8)/pH 8.1/pH 8.5/pH 9.5. W2.3: 800 g of woad leaves soaked for 12 h in 4.5 l of water (30 °C, incubator), leaves removed. Liquid divided into 4 dye baths (each 1.1 l) at different pH levels: without adding potash (pH 5.5)/pH 8.1/pH 8.5/pH 9.5. W2.4: 800 g of woad leaves soaked for 24 h in 4.5 l of water (30 °C, incubator), leaves removed. Liquid divided into 4 dye baths (each 1.1 l) at different pH levels: without adding potash (pH 4.7)/pH 8.1/pH 8.5/pH 9.5. W2.5: 1.6 l water (60 °C) poured over 800 g of leaves, then 2.9 l water (24 °C) added (temperature of mixed water: 31 °C). 0.5 l of vinegar were added (resulting in pH 3.5 of liquid). Kept for 24 h at room temperature (24–25 °C). Leaves removed, liquid divided into 4 dye baths, at different pH levels: without adding potash (pH 4.0)/pH 8.1 (?)/pH 8.5 (?) W2.6: 800 g of woad leaves soaked for 24 h in 4.5 l of water (35 °C, incubator), leaves removed. Liquid divided into 4 dye baths (each 1.1 l) at different pH levels: without adding potash (pH 4.7)/pH 8.1/pH 8.5/pH 9.5. pH measured with Merck pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, Special indicator)	W2.1, W2.2, W2.3, W2.4, W2.5: in each dye bath, 2 samples were dyed at 30 °C (incubator): one sample with 1 dipping (0.5 h dipping, 0.5 h aerating) and one sample with 2 dippings (each dipping: 0.5 h dipping, 0.5 h aerating). W2.6: same as others, but dyeing at 35 °C. Sample size: W2.1: each sample 20 g W2.2, W2.3, W2.4, W2.5, W2.6: each sample 10 g.	24	46

(continued on next page)

Table B.1 (continued)

Series	Dye baths prepared per series	Preparation per jar	Dyeing	No. dye baths	No. samples
W0 ^b pigment first harvest	W0.2: soaking 24 h, filtering off, pH 8.3 W0.3: same liquid as W0.2, but pH raised further to pH 8.5 W0.4: same liquid as W0.3	Preparation of liquid for pigment production: 15.5 kg fresh leaves soaked in 64 l of water for 24 h (water temperature at the beginning 35 °C, container kept outside in the sun), leaves removed. PH raised with potash from pH 4.7 to pH 8.3. Dyeing of W0.2 (see next column). PH raised further to pH 8.5, dyeing of W0.3 and W0.4 (water temperature during dyeing: 35 °C) pH measured with <i>Merck</i> pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, Special indicator)	W0.2: 1 dipping (0.5 h dipping, 0.5 h aerating) = SAMPLE 1 W0.3: 1 dipping (0.5 h dipping, 0.5 h aerating) W0.4: 2 dippings (each dipping: 0.5 h dipping, 0.5 h aerating) = SAMPLE 2 <i>Sample size:</i> W0.2: sample 20 g W0.3, W0.4: sample 10 g.	1	3
W0 ^b pigment second harvest	W0.5: soaking 20 h, removing leaves, pH 9–10 W0.6: same liquid as W0.5	Preparation of liquid for pigment production: 18 l of water (60 °C) poured over 9.0 kg fresh leaves, then 30 l of water (20 °C) added, resulting in water temperature of 30 °C. Soaked for 20 h, leaves removed. PH raised with potash from pH 4.7 to pH 9–10. Dyeing of W0.5 and W0.6 (see next column). pH measured with <i>Merck</i> pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, Special indicator)	W0.5: 1 dipping (0.5 h dipping, 0.5 h aerating) W0.6: 2 dippings (each dipping: 0.5 h dipping, 0.5 h aerating) <i>Sample size:</i> each sample 10 g.	1	2
Repro ^c Optimal method	analogous to W2.2 at pH 8.3	1000 g leaves soaked for 6 h in 4.4 l water (30 °C, incubator), leaves removed, pH raised with potash from pH 5.8 to pH 8.3 (water temperature during dyeing: ~27 °C) pH measured with <i>Merck</i> pH-indicator strips (pH 2.0–9.0; pH 0–14, Universal indicator; pH 4.0–7.0 and pH 6.5–10, Special indicator)	Dyeing 2 dippings (= SAMPLE 3) and 4 dippings (= SAMPLE 4), each dipping: 0.5 h dipping, 0.5 h aerating. <i>Sample size:</i> each sample 20 g (consisting of 10 g machine-spun merino yarn + 10 g hand-spun yarn of Montafon stone sheep wool, dyed together).	1	4
Total number of dye baths/samples				32	73

Notes:

SAMPLE + number indicates the samples analysed by HPLC-PDA.

^a Following a recommendation by David Hill (University of Bristol, UK) personal communication per email, 13 August 2010.

^b The dyeings were performed during pigment production with the first and second leaf harvest (see also Table 4), before the liquid was aerated. The experiments are labelled in chronological order; W0.1: another experiment testing a technique with fresh leaves and vinegar, analogous to dyer's knotweed, not relevant here.

^c The remark "repro" indicates the series performed with hand-spun yarns for the ribbon reproductions.

Table B.2

Dyeing with green and couched woad.

Series ^a	Vats prepared per series	Preparation per jar according to Cardon, (2007); Edmonds, (1998b), adapted	Process control	Dyeing ^b	Duration (days)	No. vats	No. samples
V4	V4.1: green woad balls from fermented pulp, 1st harvest V4.2: green woad balls from fresh pulp, 1st harvest V4.3: green woad balls from fermented pulp, 2nd harvest V4.4: green woad balls from fresh pulp, 2nd harvest V4.5: pounded and dried leaf pulp, 2nd harvest	All vats: 133.33 g woad + 1.3 l water (90 °C) mixed, left to cool down to 50 °C. pH measured and raised with potash to ca. pH 9.0–9.5; Kept in water bath at 50 °C.	All vats: controlled and stirred twice a day, adjusting ca. pH 9.0–9.5 with potash. vats abandoned on 2nd and 5th day because fermentation too strong. pH measured with pH tester of Hanna Instruments HI 98127.	No samples dyed	5	5	0
V5	V5.1: green woad balls from fermented pulp, 1st harvest V5.2: green woad balls from fresh pulp, 1st harvest V5.3: green woad balls from fermented pulp, 2nd harvest V5.4: green woad balls from fresh pulp, 2nd harvest V5.5: couched woad from pre-experiment 2009 (woad balls of fresh pulp)	All vats: 50 g woad + 1 l water (80 °C) mixed, left to cool down to 50 °C. pH measured and raised with potash to ca. pH 9.5. Kept in water bath at 50 °C.	All vats: controlled and stirred 3 times on the 1st day, then 2 times per day, adjusting ca. pH 9.0–9.5 with potash. pH measured with pH tester of Hanna Instruments HI 98127.	3rd day, in V5.4 and V5.5: 1 dipping (3 h dipping, 0.5 h aerating); 4th day, first dyeing, in all vats: 1 dipping (1 h dipping, 15 min aerating); 4th day, second dyeing, in V5.1, V5.4, and V5.5: 1 dipping (1 h dipping, 15 min aerating); 4th day, third dyeing, in V5.1 and V5.5: 1 dipping (1 h dipping, 15 min aerating). <i>Sample size:</i> each sample 5 g. Before the second dyeing on the 4th day, a piece of gauze bandage was placed on top of the plant material in every jar.	4	5	12
V6	V6.1: green woad balls from fermented pulp, 1st harvest V6.2: green woad balls from fresh pulp, 1st harvest V6.3: green woad balls from fermented pulp, 2nd harvest V6.4: green woad balls from fresh pulp, 2nd harvest	All vats: same preparation as V5	All vats: controlled and stirred 2 times on the 1st day, 4 times on the 2nd day, adjusting ca. pH 9.5 with potash. Vat abandoned on 3rd day. pH measured with pH tester of Hanna Instruments HI 98127.	3rd day, in all vats: 1 dipping (10 h dipping, 15 min aerating). Dyeing in V6.1 = SAMPLE 26 (pH during dyeing: 9.0), dyeing in V6.2 = SAMPLE 27 (pH 9.3), dyeing in V6.3 = SAMPLE 28 (pH 9.5), dyeing in V6.4 = SAMPLE 17 (pH 9.2) <i>Sample size:</i> each sample 5 g. In every jar a piece of gauze bandage was placed on top of the plant material.	3	4	4

(continued on next page)

Table B.2 (continued)

Series ^a	Vats prepared per series	Preparation per jar according to Cardon, (2007); Edmonds, (1998b), adapted	Process control	Dyeing ^b	Duration (days)	No. vats	No. samples
V10	V10.1: green woad balls from fermented pulp, 1st harvest V10.2: green woad balls from fresh pulp, 1st harvest V10.3: green woad balls from fermented pulp, 2nd harvest V10.4: green woad balls from fresh pulp, 2nd harvest V10.5: couched woad from woad balls of fresh pulp, 1st harvest V10.6: couched woad from woad balls of fresh pulp, 2nd harvest	Green woad (V10.1, V10.2, V10.3, V10.4): same preparation as V5 Couched woad (V10.5, V10.6): same preparation as V5, but 70 g couched woad	All vats: controlled and stirred 1–2 times, adjusting ca. pH 9.5 with potash, from the 5th day on no pH adjustment, just documentation. pH measured with pH tester of Hanna Instruments HI 98127.	5th day, in all vats: 1 dipping (1.5 h dipping, 0.5 h aerating). <i>Sample size:</i> each sample 5 g.	7	6	6
V12 colour ^c Optimal method	V12.1: couched woad from woad balls of fermented pulp, 1st harvest V12.2: couched woad from woad balls of fresh pulp, 1st harvest V12.3: couched woad from woad balls of fresh pulp, 2nd harvest	All vats: 70 g couched woad + 1.3 l water (80 °C) mixed, left to cool down to 50 °C. pH measured and raised with potash to pH ca. 9.0. Kept in water bath at 50 °C.	All vats: controlled and stirred 2–3 times per day, adjusting ca. pH 9.0 with potash. pH during dyeing ca. pH 8.5. On 5th day, 0.7 g wheat bran was added to each vat to enhance fermentation. pH measured with pH tester of Hanna Instruments HI 98127.	4th day, in V12.2 (dyeing blue + over dyeing two shades of red; in total 5 g): 4 dippings (each dipping: 2 h dipping, 0.5 h aerating, pH 8.5), blue = SAMPLE 6 . Before dyeing the sample, a test thread was dyed with 1 dipping (2 h dipping, 0.5 h aerating, pH 8.5) = SAMPLE 5 . 5th day: in V12.1 (dyeing blue + over dyeing two shades of yellow; in total 5 g): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating), in V12.2 (dyeing blue + over dyeing two shades of yellow; in total 5 g): 4 dippings (each dipping: 2 h dipping, 0.5 h aerating), in V12.3 (dyeing blue + over dyeing two shades of red; in total 5 g): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating, pH 8.4), blue = SAMPLE 8 . Before dyeing the sample, a test thread was dyed in V12.3 with 1 dipping (2 h dipping, 0.5 h aerating, pH 8.4) = SAMPLE 7 . 6th day, in all vats: 1 dipping (2 h dipping, 0.5 h aerating), each sample 5 g. Before the dyeing on the 6th day, a piece of gauze bandage was placed on top of the plant material.	6	3	7 blue + 8 over dyeings
Total number of vats/samples (without over dyeings)						23	29

Notes:

SAMPLE + number indicates the samples analysed by HPLC-PDA.

^a All vat series (green and couched woad vats as well as vats with woad pigment and indigo) were numbered chronologically (V1, V2 etc.). The missing numbers in this table are vats with woad pigment or indigo and are therefore documented in Table B.3.

^b Dyeing: the textile is immersed in the vat. After taking it out, it is exposed to air to enable the oxidising of indigotin (aerating). The whole procedure is called one dipping and can be repeated to build up darker shades (e.g. repeating 4 times = 4 dippings).

^c The remark “colour” indicates the series performed to dye a colour palette to select colour shades for the ribbon reproductions (publication in preparation). Two shades of red wool (dyed with madder, *Rubia tinctorum* L.) and yellow wool (dyed with scentless chamomile, *Tripleurospermum inodorum* L.) were over dyed in the vat, always together with a sample of white wool (in total 5 g wool per dyeing).

Table B.3Dyeing with woad pigment and indigo from *Indigofera* spp. (urine and potash–madder–bran vats).

Series ^a	Vats prepared per series	Preparation per jar	Process control	Dyeing ^b	Duration (days)	No. vats	No. samples
V1 urine	V1.1: indigo Galke, “new” urine V1.2: indigo Galke, “old” urine V1.3: indigo Kremer, “old” urine V1.4: indigo Kremer, “new” urine V1.5: indigo Galke, “old” urine V1.6: indigo Kremer, “old” urine	According to Cardon, (2007); Grierson, (1989); Nencki, (1984); Spränger, (1975); Fischer, (1999): Preparation of fermented urine: “old” urine: urine collected for 19 days and kept at room temperature for 24 days; “new” urine: collected during the days just before filtering off. For each vat: 1 l urine filtered through cotton fabric and kept in water bath at 40 °C. Urine fermented for 14 days (V1.1., V1.2, V1.3) and 20 days (V1.4, V1.5, V1.6) respectively. Preparation of vat: V1.1., V1.2, V1.3: 2.5 g indigo added to 1 l urine after fermentation for 14 days. V1.4, V1.5, V1.6: 2.5 g indigo added to 1 l urine after fermentation for 20 days. Kept in water bath at 40 °C.	Controlling of urine fermentation: pH measured daily with pH-indicator strips for urine, pH 2.0–9.0 (<i>Merck</i>). Occasionally stirred and changes documented (colour, mould, dull skin, smell). If mould occurred, it was removed. Controlling of all vats: stirred daily and changes documented (colour, mould, dull skin, smell, white sediment on the bottom of the jar). If mould occurred, it was removed. Trials to enhance fermentation: little pieces of madder roots added on 13th day of the vat process (V1.1, V1.2, V1.3); a small spoon of brown sugar added on the 20th (V1.1), 30th (V1.1, V1.3) and 48th day (V1.3) of the vat (days counted since indigo added to urine). Vats abandoned after 14 days (V1.4, V1.5, V1.6), 42 days (V1.1, V1.2) and 55 days (V1.3) due to stagnation and insufficient dyeing results (days counted since indigo added to urine).	12th day, in V1.1, V1.2 and V1.3: 1 dipping (12 h dipping and 1.5 h aerating). 24th day, in V1.1, V1.2 and V1.3: 1 dipping (10 h dipping and 0.5 h aerating). 30th day, in V1.2: 1 dipping (0.5 h dipping and 0.5 h aerating). 35th day, in V1.3: 1 and 2 dippings (each dipping: 0.5 h dipping and 0.5 h aerating). 39th day, in V1.3: 3 dippings (each dipping: 0.25 h dipping and 0.5 h aerating). Days counted since indigo added to urine. <i>Sample size:</i> each sample 5 g.	93 (max. 44 days urine fermentation + max. 55 days for vat)	6	10
V14 urine	V14.1: indigo Galke V14.2: woad pigment, 1st harvest	According to Cardon, (2007); Grierson, (1989); Nencki, (1984); Spränger, (1975); Fischer, (1999), adapted: Preparation of fermented urine: urine collected for 6 days and kept at room temperature for 2 days. Then kept in water bath at 40 °C for 10 days. Preparation of vat: fermented urine filtered through cotton fabric. V14.1: 3.2 g indigo added to 1 l fermented urine. V14.2: 6.4 g woad pigment from 1st harvest added to 1 l fermented urine. Kept in water bath at 40 °C.	Controlling of urine fermentation: pH measured daily with pH-indicator strips for urine, pH 2.0–9.0 (<i>Merck</i>). Changes documented (colour, white sediment on the bottom of the jar). Controlling of all vats: stirred and changes documented daily (colour, smell, skin/flower, bubbles, colour of wooden brochettes used for stirring, colour of liquid in the jar and in glass pipette), from 15th day on stirred daily and changes documented every second day. pH measured with pH-indicator strips for urine, pH 2.0–9.0 (<i>Merck</i>) and pH tester of <i>Hanna Instruments HI 98127</i> . Temperature of water bath reduced to 30 °C on 9th day, increased to 40 °C again on 39th day. Vats abandoned after 75 days due to stagnation and insufficient dyeing results (days counted since indigo added to urine).	34th day, in V14.1: 1 dipping (12 h dipping and 0.5 h aerating). 64th day, in V14.1 and V14.2: 1 dipping (12 h dipping and 0.5 h aerating). 74th day, in V14.1 and V14.2: 1 dipping (12 h dipping and 0.5 h aerating). Days counted since indigo added to urine. <i>Sample size:</i> each sample 5 g.	84 (10 days urine fermentation + 75 days for vat)	2	5
V2	V2.1: indigo Galke, recipe according to <i>Spränger, (1975)</i> V2.2: indigo Galke, according to <i>Spränger, (1975)</i> , modified V2.3: indigo Kremer, according to <i>Spränger, (1975)</i> V2.4: indigo Kremer, according to <i>Spränger, (1975)</i> , modified	V2.1 and V2.3 according to Spränger, (1975): 1.6 g madder + 1.6 g wheat bran mixed with 1.3 l water (80 °C), kept in water bath at 80 °C for 4 h; 4.9 g potash added and left to cool down to 40 °C (resulted in pH 11); 3.25 g indigo added, kept in water bath at 40 °C. 2nd and 3rd day not stirred, then stirred twice a day. V2.2 and V2.4 according to Spränger, (1975), modified: same preparation, but stirred twice every day.	All vats: controlled once a day, stirred twice a day (except V2.1 and V2.3: no stirring at 2nd and 3rd day). Vats abandoned on 9th day due to mould. pH measured with pH-indicator strips pH 0–14, universal indicator (<i>Merck</i>).	5th day, in V2.1 and V2.2: in each vat 1 and 2 dippings (each dipping: 0.5 h dipping and 0.5 h aerating). <i>Sample size:</i> each sample 5 g.	9	4	4

(continued on next page)

Table B.3 (continued)

Series ^a	Vats prepared per series	Preparation per jar	Process control	Dyeing ^b	Duration (days)	No. vats	No. samples
V3	V3.1: indigo Galke, according to Spränger, (1975) , adapted V3.2: indigo Kremer, according to Spränger, (1975) , adapted V3.3: indigo Galke, according to Melvin, (2007) and Melvin (2010) ^c V3.4: indigo Kremer, according to Melvin, (2007) and Melvin (2010) ^c	V3.1 and V3.2 according to Spränger, (1975), adapted: 1.6 g madder + 1.6 g wheat bran mixed with 1.3 l water (80 °C), kept in water bath at 80 °C for 4 h; left to cool down to 40 °C and adjust pH 9–10 with potash, 3.25 g indigo added, kept in water bath at 40 °C. V3.3 and V3.4 according to Melvin, (2007) and workshop Melvin (2010)^c: 8.7 g madder + 2.9 g wheat bran mixed with 1.3 l water, pH 9–10 adjusted with potash, boiled for 15 min in water bath, left to cool down to 40 °C, 3.2 g indigo added, kept in water bath at 40 °C.	All vats: controlled and stirred twice a day; adjusting ca. pH 9–10 with potash, during dyeing ca. pH 8–9. To stimulate fermentation in V3.1 and V3.2, wheat bran was added at the 5th and 7th day (0.7 g bran each vat and each day). pH measured with pH-indicator strips pH 0–14, universal indicator (<i>Merck</i>).	4th day, in all vats: 1 dipping (0.5 h dipping and 1 h aerating); 6th, 8th and 10th day, in all vats: 1 dipping (0.5 h dipping and 0.5 h aerating). <i>Sample size:</i> each sample 5 g.	10	4	16
V7	V7.1: indigo Galke V7.2: indigo Kremer V7.3: woad pigment 1st harvest V7.4: woad pigment 2nd harvest V7.5: woad pigment 1st harvest, potash added later V7.6: woad pigment 2nd harvest, potash added later	According to Melvin, (2007) and workshop Melvin (2010)^c: V7.1–V7.4: same preparation as V3.3 and V3.4, ca. pH 9.5 was adjusted with potash V7.5, V7.6: same preparation as V3.3 and V3.4, but pH was adjusted after the woad pigment was added (because the pH of the woad pigment was not known).	All vats: controlled and stirred twice a day; adjusting ca. pH 9.5 with potash. Vat abandoned on 3rd day because of too strong pH fluctuation. pH measured with pH tester of <i>Hanna Instruments HI 98127</i> .	3rd day, in all vats: 1 dipping (1 h dipping and 0.5 h aerating). <i>Sample size:</i> each sample 5 g.	3	6	6
V8	V8.1: indigo Galke V8.2: indigo Kremer V8.3: woad pigment 1st harvest V8.4: woad pigment 2nd harvest	According to Melvin, (2007) and workshop Melvin (2010)^c: same preparation as V3.3 and V3.4, ca. pH 9.5 was adjusted with potash.	All vats: controlled and stirred 2–3 times a day; adjusting ca. pH 9.5 with potash. Vat abandoned on 4th day. pH measured with pH tester of <i>Hanna Instruments HI 98127</i> .	2nd day, first dyeing, in all vats: 1 dipping (1 h dipping, 0.5 h aerating). Dyeing in V8.4 (pH 7.0) = SAMPLE 16 . 2nd day, second dyeing, in all vats: 1 dipping (0.5 h dipping, 0.5 h aerating). 4th day, in all vats: 1 dipping (12 h dipping and 0.5 h aerating). <i>Sample size:</i> each sample 5 g.	4	4	12
V9	V9.1: indigo Galke (V9.2: indigo Kremer, jar broke during preparation) V9.3: woad pigment 1st harvest V9.4: woad pigment 2nd harvest	According to Melvin, (2007) and workshop Melvin (2010)^c, adapted: Indigo vats (V9.1, V9.2): same preparation as V3.3 and V3.4, ca. pH 9.5 was adjusted with potash. Woad pigment vats (V9.3, V9.4): same preparation as V3.3 and V3.4, but double amount of woad pigment (6.4 g), ca. pH 9.5 was adjusted with potash.	All vats: controlled and stirred 3 times a day; adjusting ca. pH 9.5 with potash. From the 3rd day on, pH control and stirring 2 times a day. No further pH adjustment was made because the strong pH fluctuation stopped, the pH declined only slowly from ca. pH 9 to minimum pH 8.2 on the 7th day. pH measured with pH tester of <i>Hanna Instruments HI 98127</i> .	3rd day, in all vats: 1 dipping (2 h dipping, 0.5 h aerating); each sample 5 g. 4th day, in all vats: 1 dipping (2 h dipping, 0.5 h aerating); each sample 5 g. 6th day, in all vats: 1–5 dippings (each dipping: 2 h dipping, 0.5 h aerating); each sample 1 g. Explanation for one vat: 1st dipping: 5 samples each 1 g were dyed together, 2nd dipping: 4 samples were dipped again, 3rd dipping: 3 samples were dipped again, 4th dipping: 2 samples were dipped again, 5th dipping: 1 sample was dipped again. Dyeing in V9.1 (pH 8.6): 1 dipping = SAMPLE 21 , 5 dippings = SAMPLE 9 . Dyeing in V9.3 (pH 8.4): 1 dipping = SAMPLE 22 , 5 dippings = SAMPLE 10 . Dyeing in V9.4 (pH 8.5): 1 dipping = SAMPLE 23 , 5 dippings = SAMPLE 11 . 7th day, in all vats: 1 dipping (2 h dipping, 0.5 h aerating); each sample 5 g.	7	4	24
V11 colour ^d	V11.1: woad pigment 1st harvest V11.2: woad pigment 2nd harvest V11.3: indigo Galke	According to Melvin, (2007) and workshop Melvin (2010)^c, adapted: Woad pigment vats (V11.1, V11.2): same preparation as V3.3 and V3.4, but double	All vats: controlled and stirred 2 times a day; adjusting ca. pH 9.5 with potash. From the 4th day on, no pH-adjustment was done any more because the strong pH fluctuation in	3rd day, in V11.1: test thread dyed (2 h dipping, 0.5 h aerating, pH 8.8) = SAMPLE 12 ; in V11.2: test thread dyed (2 h dipping, 0.5 h aerating, pH 8.3) = SAMPLE 13 ; in	9	4	8 blue + 8 overdyings

	V11.4: madder/bran without indigo or woad (controll variant)	amount of woad pigment (6.4 g), ca. pH 9.5 was adjusted with potash. Indigo vat (V11.3): same preparation as V3.3 and V3.4, ca. pH 9.5 was adjusted with potash. Madder/bran (V11.4): same preparation as V3.3 and V3.4, but without indigo or woad, ca. pH 9.5 was adjusted with potash.	the woad/indigo vats stopped, the pH declined slowly from ca. pH 9 to minimum pH 8.2 on the 9th day. To stimulate fermentation in V11.1 and V11.3, wheat bran was added at the 6th day (0.7 g bran each vat). pH measured with pH tester of <i>Hanna Instruments HI 98127</i> .	V11.3: test thread dyed (2 h dipping, 0.5 h aerating, pH 8.9) = SAMPLE 14 ; in V11.4: test thread dyed (2 h dipping, 0.5 h aerating, pH 6.3) = SAMPLE 15 . 5th day, in all vats: 1 dipping (2 h dipping, 0.5 h aerating); each sample 5 g. 6th day, in V11.2 (dyeing blue + overdyeing two shades of red; in total 5 g): 4 dippings (each dipping: 2 h dipping, 0.5 h aerating); 7th day, in V11.2 (dyeing blue + overdyeing two shades of yellow; in total 5 g): 4 dippings (each dipping: 2 h dipping, 0.5 h aerating); 8th day, in V11.2 (dyeing blue + overdyeing two shades of red; in total 5 g; blue + overdyeing two shades of yellow; in total 5 g): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating). Dyeing of hand-spun yarn for reproductions: 3rd day, in V13.1 (overdyeing red): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating); 4th day, in V13.1 (continuing with overdyeing red): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating); and in V13.2 (dyeing blue and overdyeing yellow): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating); 5th day, in V13.2 (continuing overdyeing yellow): 1dipping (2 h dipping, 0.5 h aerating); 6th day, in V13.2 (continuing overdyeing red): 1 dipping (2 h dipping, 0.5 h aerating). Dyeing of hand-spun yarn for reproductions: 4th day, in V15.1 (overdyeing yellow) and in V15.2 (dyeing blue): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating); 5th day, in V15.1 (continuing overdyeing yellow): 1 dipping (2 h dipping, 0.5 h aerating); and in V15.2 (continuing dyeing blue): 2 dippings (each dipping: 2 h dipping, 0.5 h aerating).	6	2	1 blue + 2 overdyeings
V13 repro ^e Optimal method	V13.1: woad pigment 1st harvest V13.2: woad pigment 2nd harvest	According to Melvin, (2007) and workshop Melvin (2010)^c, adapted: same preparation as V3.3 and V3.4, but double amount of woad pigment (6.4 g), and ca. pH 9.0 was adjusted with potash.	All vats: controlled and stirred 2 times a day; adjusting ca. pH 9.0 with potash. From the 4th day on, no further pH adjustment was made because the pH fluctuation stopped, the pH kept stable at ca. pH 8.5 until the 6th day. pH measured with pH-indicator strips: pH 0–14, universal indicator (<i>Merck</i>) and colour-fixed inicator sticks pH-fix 2.0–9.0 (<i>Macherey-Nagel</i>).				
V15 repro ^e Optimal method	V15.1: woad pigment 1st harvest V15.2: woad pigment 2nd harvest	According to Melvin, (2007) and workshop Melvin (2010)^c, adapted: same preparation as V3.3 and V3.4, but double amount of woad pigment (6.4 g), and ca. pH 9.0 was adjusted with potash.	All vats: controlled and stirred 2 times a day; adjusting ca. pH 9.0 with potash. On the 5th day no further pH adjustment was made because the pH fluctuation stopped, the pH kept stable at ca. pH 8.5 pH measured with pH-indicator strips: pH 0–14, universal indicator (<i>Merck</i>) and colour-fixed inicator sticks pH-fix 2.0–9.0 (<i>Macherey-Nagel</i>).	5	2	1 blue + 1 overdyeing	
Total number of vats/samples (without overdyeings)					38	87	

Notes:

SAMPLE + number indicates the samples analysed by HPLC-PDA.

^a All vat series (green and couched woad vats as well as vats with woad pigment and indigo) were numbered chronologically (V1, V2, etc.). The missing numbers in this table are vats with green woad or couched woad and are therefore documented in Table B.2.

^b Dyeing: the textile is immersed in the vat. After taking it out, it is exposed to air to enable the oxidising of indigotin (aerating). The whole procedure is called one dipping and can be repeated to build up darker shades (e.g. repeating 4 times = 4 dippings).

^c Workshop Melvin 2010: workshop for A. Hartl by Helen Melvin, artist and dyer in Bodfari, Denbigshire, UK, 28–30.09.2010.

^d The remark "colour" indicates the series performed to dye a colour palette to select colour shades for the ribbon reproductions (publication in preparation). Two shades of red wool (dyed with madder, *Rubia tinctorum* L.) and yellow wool (dyed with scentless chamomile, *Tripleurospermum inodorum* L.) were overdyed in the vat, always with a sample of white wool (in total 5 g of wool per dyeing).

^e The remark "repro" indicates the series performed with hand-spun yarns for the ribbon reproductions.

Appendix C. Spectra of unknown components analysed

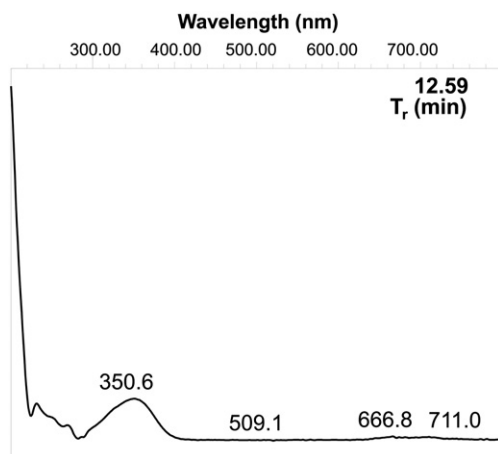
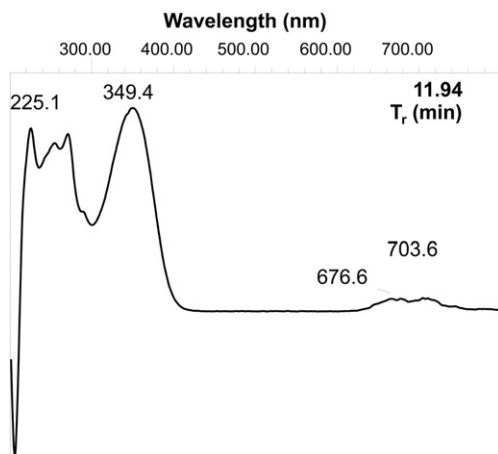
Fig. C.1. Unknown component related to soap wort (*Saponaria officinalis* L.).

Fig. C.2. Yellow flavonoid W349. Absorption profile at pH 3. Note: this component is halochromic.

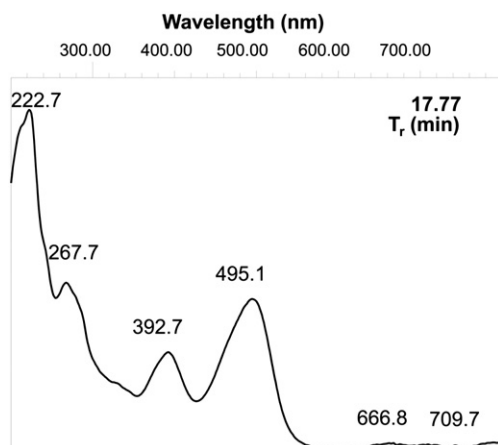


Fig. C.3. Unknown red component W495.

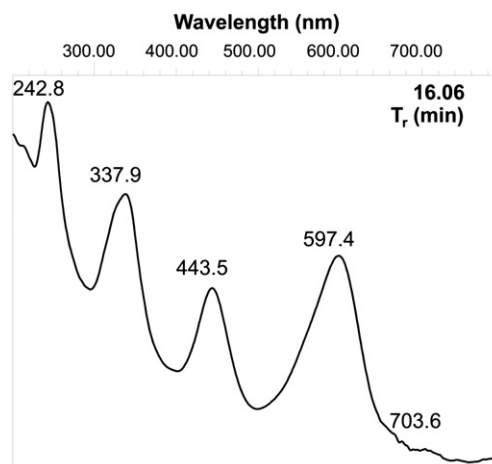


Fig. C.4. Unknown light cyan component W597.

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