

Dyes in History and Archaeology: the early years

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Abstract The formation of a group of researchers interested in the use of dyes on historical and archaeological textiles was due to two people working in that field, George Taylor and Penelope Walton Rogers. From its first meeting in 1982, which consisted of eight people, the group has grown in numbers and has become international in its still very informal membership. The subject matter was extended to include dyes used in pigments and over the years different techniques for the analysis of dyes, both as raw materials and in textiles and pigments, have been described and discussed. The group acts as an academic forum for discussion of all aspects of the use and examination of historical dyes. The author was invited to contribute this paper to celebrate the 25th anniversary of the *Dyes in History and Archaeology* (DHA) research group. It was read before the reception and banquet held to commemorate the event, 21 September 2006.

The formation of *Dyes in History and Archaeology* (DHA) was due principally to the foresight and imagination of two people, George Taylor (Fig. 2) and Penelope Walton who is now known as Penelope Walton Rogers, Pen to her friends. In 1980 Pen was a freelance field archaeologist and

artefact researcher who was working on a batch of excavated textiles (Fig. 3). In order to identify the dyes she approached Mark Whiting at the University of Bristol's Chemistry Department. Mark was also receiving textiles for dye analysis from other archaeologists, therefore had experience in this type of work.

George Taylor had recently retired as research director of the Fibres Division of Imperial Chemical Industries (ICI) at its headquarters at Harrogate. At that time ICI was one of the largest and most prestigious companies in the UK. Having taken early retirement, George was looking for something to occupy himself. At the time the Viking excavations at York were very active so he wrote to the York Archaeological Trust (YAT) to offer his services. Although he was turned down, Pen, who occasionally worked for YAT, heard of his offer and asked him if he could work on dye analysis with her instead. Mark Whiting was able to show George his techniques and other workers interested in dye analysis in the UK were



Figure 1 Jan Wouters and Jo Kirby cutting the DHA 25th Anniversary cake during the celebration banquet in 2006. Photo © Ileana Cretu and Mihai Lupu.

contacted including Nick Eastaugh, then at the Textile Conservation Centre at Hampton Court Palace (and now a freelance analyst working principally on painted artefacts), Helen Dalrymple, a conservation scientist at the National Museum of Antiquities of Scotland (Helen, incidentally, was Anita Quye's predecessor in the laboratory at what is now the National Museums Scotland), David Duff and Roy Sinclair at the Paisley College of Technology and Su Grierson (Fig. 4) an independent part-time dyer.

In the 1980s the methods used for dye analysis were less sophisticated than those available now and key workers often favoured different techniques. As far as the UK was concerned, the most prominent researcher in this field was Mark Whiting who complemented his interest in the analysis of natural dyes by being a keen collector of oriental carpets. As early as 1979, he was publishing articles on the dyes in carpets, which had been analysed using a variety of techniques including differential solubility in solvents and mass spectroscopy.¹ With his research student John Harvey, his group was to be the first in the UK to routinely use high performance liquid chromatography (HPLC) for the analysis of natural dyes.

Elsewhere, in the 1970s, Helmut Schweppe in Germany was using mainly acid extraction followed by thin layer chromatography (TLC), often on a polyamide plate.² Max Saltzman in the USA (shown in Fig. 5 with Helmut Schweppe) was measuring the spectra of dyes in solution (and his interest in and involvement with natural dyes went back even longer to 1961);³ he was able to exploit the fact that the solutions of dyed textiles in concentrated sulphuric acid yielded strong and characteristic spectra in the UV-visible (UV-Vis) region, a method which has since fallen out of use. In the Netherlands, Judith Hofenk de Graaff (shown in Fig. 6 with Jan Wouters) and Wilma Roelofs were measuring infrared spectra and investigating TLC from the late 1960s and 70s.⁴ Preliminary work at the York laboratory favoured the use of acid extraction of dyes followed by UV-Vis transmission spectroscopy of the solution, often followed by re-measuring the spectrum after the addition of magnesium acetate solution; TLC was also used.⁵



Figure 2 George Taylor in 2006. Photo © Vincent Daniels.



Figure 3 Penelope Walton at work on archaeological textile fragments in the 1980s. Photo © Penelope Walton Rogers.



Figure 4 Su Grierson, *Glacier*, an installation at Yokohama Museum, Japan, 2003. Photo © Su Grierson.



Figure 5 Helmut Schweppe (left) and Max Saltzman (right) at the 7th DHA meeting, York, 1988. Photo © Vincent Daniels.



Figure 6 Judith Hofenk de Graaff with Jan Wouters at lunch, DHA 21, Avignon, October 2002. Photo © Rolf Haubrichs.

At the National Gallery in the 1970s Jo Kirby and Raymond White (Fig. 7) were extracting dyes from pigments using boron trifluoride in methanol and identifying the dyes using TLC on plates spread with a mixture of acetylated cellulose with a little polyamide. Jo was also attempting to identify lake pigments by transmittance microspectrophotometry of pigment particles or very thin paint cross-sections.⁶

In 1981 Pen and George thought that a one-off meeting of people interested in dye analysis on archaeological and historic textiles would be a good thing. This took place on 20 August 1982 at King's Manor, part of the University of York. The level of interest and enthusiasm was so high that participants decided to repeat the event and so DHA was born. The name of the group, *Dyes on Historical and Archaeological Textiles* (DHAT), changed to *Dyes in History and Archaeology* (DHA) at the seventh meeting, also held in York in 1988. The proceedings of the first meeting were published by the National Museum of Antiquities of Scotland and edited by Helen Dalrymple.⁷ The 16-page pamphlet was described as a 'summary of talks' and was priced at £1.00. It was decided that Helen would host the next meeting in Edinburgh, but that alternate meetings would be held at York, thus all the DHA meetings with odd numbers were held at York up to the 11th session. At this stage the numbers of delegates became too large for the available venues. Since then, DHA has never returned to York (a situation which one day may be rectified).

At the first conference, each of the eight delegates presented papers. The subjects discussed give an idea of the character of the meetings and the state of dye studies at the time. Mark Whiting described recent work on the UV-Vis analysis of dyes, including the use of zirconium chelates for the analysis of flavonoids eluted from HPLC apparatus. It is useful to remember that diode array detection (DAD) of such fractions was not possible in 1982 and that HPLC was a more novel and difficult technique for dye analysis than it is now. John Harvey (who had previously worked for Mark Whiting and then for the Mary Rose Trust) described the



Figure 7 Jo Kirby and Raymond White in the laboratory at The National Gallery, London, 1974. Photo: John Donat. © The National Gallery, London. Reproduced by permission of the National Gallery, London.

use of acid extraction of textile dyes and analysis of the solutions by UV-Vis spectroscopy and TLC on acetylated cellulose or polyamide plates followed by development of the spots.

George Taylor, who was to attend meetings for a further 20 years, spoke on the success of analysing indigo, orchil and madder on Anglo-Scandinavian textiles from excavations at York and Penelope Walton discussed the successful identification of 17th-century dyes as well as the wide range of dyes that could be extracted from textiles which were brown in appearance. After analysing 60 samples conclusions could be drawn on the use of dyes in this period. Roy Sinclair and David Duff, from the Paisley College of Technology, provided DHA with valuable input on scientific and technical aspects of the dyeing industry both at this meeting and for several years subsequently. On this first occasion, Roy Sinclair spoke about methods of measuring colour and current work on the fading of natural dyes, while David Duff discussed studies on Scottish dyes.

Helen Dalrymple from the National Museum of Antiquities of Scotland discussed the wide range of types of dye that could be encountered in a large national museum and the use of X-ray fluorescence (XRF) to determine mordants in dyed textiles. Su Grierson played an essential



Figure 8 Frank Jones.



Figure 9 Vincent Daniels at a DHA meeting.

role in the early days of DHA as a source of well-characterised dyed textile samples. Helen and many other authors of papers included thanked Su for her assistance. Lastly, an archaeologist, Gillian Eastwood, described the types of textiles she was finding while excavating in the Middle East and offered samples to workers interested in analysing them.

The second meeting in Edinburgh welcomed Frank Jones of Leeds University (Fig. 8), who described the collection of solid crystalline and purified components of natural colouring matters assembled by A.G. Perkin as well as a collection of other dyeing materials held at the university's Department of Colour Chemistry and Dyeing. Frank became an enthusiastic supporter of DHA and later hosted DHA 6 at the University of Leeds. George and Pen described their considerable advances into dye analysis of shellfish and lichen dyes: the subject of shellfish purples is one which has since recurred every year at DHA meetings. Vincent Daniels (Fig. 9) of the British Museum, now the longest serving active member of DHA, also spoke of the first attempts to undertake dye analysis at the museum.

In York, the following year, Su Grierson announced her intention to photograph, catalogue, carry out test dyeings and generally research the Leeds dye collections. This became known as the Leeds Dye Project and the completed work was described at the 25th meeting. George Taylor gave the first DHA paper on insect red dyes, which helped members to navigate a bewildering field of study. Subsequent meetings were to see further lectures by him which helped to clarify what were, at that time, confusing natural dye themes: insect dyes were to become a regular subject of all subsequent meetings. Dye analysis at York had continued to develop well and kermes, lichen and saffron were reported to have been added to the range of dyes found in medieval textiles.

At the 4th meeting at the British Museum hosted by Vincent Daniels, Jo Kirby and Raymond White attended for the first time and this was also the first opportunity to hear a paper on anthocyanin dyes given by

Su Grierson. At the 5th meeting back at York delegates continued to hear of improvements in working methods. George Taylor presented a paper on the analysis of dyes from dyewoods by UV-Vis spectroscopy of extracts from dyed yarn. A lecture by Michael Ryder on natural pigmentation of animal textile fibres was given and Helen Garland (previously Helen Dalrymple) was the first regular DHA attendee to submit a paper on the analysis of dyes by HPLC, in this case madder and its constituent hydroxyanthraquinones. The method of analysis was based on that developed by Jan Wouters (and published as a seminal article in 1985);⁸ Jan became a DHA member at that meeting and delivered a paper on the colouring matter of *Rhus cotinus*. Published in the proceedings of DHA 6, this was a landmark paper showing how modern instrumental analytical techniques could be utilised to increase the quality of results obtained by dye analysis. At that time analysis of a wide range of dyes was carried out using HPLC by Wouters and co-workers at the Koninklijk Instituut voor het Kunstpatrimonium (Royal Institute for Cultural Heritage) in Brussels. This paper discussed not only analysis of dyed yarn by HPLC, but also identification of an unknown peak by isolating the compound responsible and performing nuclear magnetic resonance spectroscopy (NMR) on it. Furthermore, dyed textile was faded artificially and the relative rates of change of the components noted.

Judith Hofenk de Graaff, with her colleague Wilma Roelofs, at what was then the Centraal Laboratorium in Amsterdam and is now the ICN (Instituut Collectie Nederland),⁹ had been active in natural dye studies for many years and had written three substantial reports for the Textiles Group of the International Council of Museums-Conservation Committee (ICOM-CC) in the late 1960s and early 70s; these were to be later revised and incorporated into an important book on natural dyes.¹⁰ Judith in particular was to become a fairly regular attendee at DHA meetings until both she and Wilma retired in 2000/2001. Many DHA members may remember the 20th meeting of DHA in Amsterdam,



Figure 10 The cover of the *DHA7 Proceedings*. Photo © Vincent Daniels.

which coincided with Wilma's retirement and could be said to have been a commemoration of both women's contribution to the field.

The 6th meeting in Leeds included two papers on insect reds: from George Taylor on kermes and one from Jan Wouters and André Verhecken (another regular contributor to DHA to this day) on HPLC of insect reds, in particular 'ordinary', Polish and Armenian cochineal. This meeting was also the first at which Jo Kirby, senior scientific officer in the Scientific Department at the National Gallery in London, spoke. The occasion was important because her lecture opened up a whole new area for consideration by DHA members – that of lake pigments. She later became editor of the proceedings of the DHA meetings from DHA 16 onwards. Sadly, Frank Jones died before the next meeting.

At the instigation of Penelope Walton, the name of the group changed to *Dyes in History and Archaeology* at the 7th meeting and the proceedings (published by Pen's own company, Textile

Research Associates) were given a glossy coloured cover (Fig. 10). From this time, contributions to the proceedings were peer reviewed. The cover of DHA 7 shows a photograph of an adult female kermes insect provided by Dominique Cardon, who delivered a lecture on kermes describing her two field trips in France and another in Turkey. This was a meeting made momentous by the presence of the distinguished dye chemist Helmut Schweppe, who gave a paper on his TLC techniques for red dyes. Another first was a lecture by George Taylor on the analysis of synthetic dyes, based on the methods already employed by natural dye analysts.

The 8th meeting held in Paisley, Scotland was hosted by Roy Sinclair, David Duff and Su Grierson. One of the most enduring memories of this meeting was the Scottish breakfasts provided by Su Grierson at Paisley College's hall of residence (and very splendid they were). Among the notable lectures given were several relating to the indigoid dyes, either in the blue form as indigo or woad, or the blue or purple brominated forms. DHA members were then still thrilled with an identification of shellfish purple on any textile. The power of HPLC, with its ability to detect strange compounds such as the partially brominated derivatives of isomers of indigotin, had yet to be unleashed on this subject. Meanwhile others concentrated on the properties of indigo that did not require HPLC. Lorna Green investigated the solvents for extracting indigo, while Vincent Daniels examined the dark fading of indigo in the dyed pages of a book.

Jenny Balfour-Paul has delighted meetings with tales of her travels in exotic locations and at the 9th meeting described her findings on indigo in the Arab world. These, together with the information gleaned from much research, formed part of her book *Indigo*.¹¹ Dominique Cardon, also the author of a book on natural dyes,¹² established the subject of black-dyed textiles and their deterioration as a new recurring theme for the group. In latter years, from DHA 14 onwards, we were to see several papers on the degradation of black-dyed New Zealand flax and visits of delegates from that country.

The growing international flavour of DHA was evident at the 10th meeting held at the National Gallery in London, hosted by Jo Kirby and Raymond White. Israel, Hungary, Japan, Belgium and France were represented in the proceedings. The meeting also broke a new record with the number of delegates exceeding 35. Indigoids were a favourite topic with four papers being submitted: Jan Wouters described the new method for HPLC of indigoids which has enabled analysts to obtain so much more information on the components present; Satoshi Ushida spoke on indigo dyeing in Japan; and Dominique Cardon produced new information on the workings of the medieval woad vat. These subjects, however, were just part of a wide ranging and fascinating programme of lectures.

It is inspiring to see that a few delegates who have retired from work on dyes have continued to attend meetings purely out of interest and to impart their experience to others. Notable among these were Max Saltzman from Los Angeles who attended the 10th meeting, then others occasionally until DHA 18. George Taylor continued to attend meetings until DHA 21 at Avignon and has since moved on to other interests.

Later meetings were to see more modern techniques applied to dye analysis: Raman spectroscopy (DHA 11, 1992); three-dimensional fluorescence spectroscopy (DHA 12); derivative UV/visible spectroscopy (DHA 16/17); liquid chromatography-ion trap mass spectroscopy (DHA 19); HPLC with fluorescence detection and thermospray liquid chromatography-mass spectroscopy (DHA 20). Some of these techniques are not easily available to the dye analyst and some may prove to have limited applicability. In contrast other researchers have made valuable contributions by finding new ways of using more easily available techniques with a wide range of applicability. Dye analysis, however, is only a minor part of any DHA programme; in other areas of study great advances are being made in our understanding of the ways dyes were used all over the world and in various historical periods.

Although delegate lists were rarely printed in DHA proceedings, some separately printed

lists have survived that show the increasing attendance and growing international flavour of the meetings. For example, DHA 9 in York had 21 delegates, only one being from outside the UK, while at DHA 15 in Manchester there were 47 delegates, 16 from outside the UK, and at DHA 12 in Brussels among 46 delegates only 10 were from the UK. It is not mandatory for all lecturers to write up their presentations for the proceedings of DHA and there are many valuable contributions, therefore, which have not been included in the published texts.

Over the years DHA has changed into a meeting where participants from all over the world meet to exchange information on the historical, economic, practical and scientific use of dyes – from preparing the fibre and dye precursors to the deterioration of the finished product. The increasing international nature of the meetings and sustained quality of contributions ensure that DHA is still the prime academic forum for technical information on natural dyes. It is, furthermore, a tribute to the fascination of the subject matter and the friendly atmosphere of the meetings that many members still attend even having left the field professionally.

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Editor's note

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