# Scientific dating of paintings

*Dr. Nicholas Eastaugh*

**Scientific dating of paintings is used by a wide range of related fields to provide independent means of verification. This paper outlines the principle approaches that are used, some problems with current methodology, and a potential solution through the application of simple mathematical modelling to the occurrences of materials and techniques in paintings. Offering a means of determining likelihood, this approach also opens up the possibility of studying economic factors involved in use and disuse of historical pigments.**

At the present time science has no reliable and accurate means for the absolute dating of a painting. Calendrical methods such as the familiar radiocarbon dating, or likewise dendrochronology ('tree-ring dating')[1] are unsuitable. Instead, much of the scientific work determining dates of paintings takes a sideways approach, relying on the identification of key pigments or techniques whose dates of introduction or disuse are known. For example, a painting that looks like a Rembrandt can't be by him if it contains the pigment Prussian blue, because that compound wasn't available until well after Rembrandt's lifetime.

This paper discusses this current methodology, outlines the basic thinking behind it and the mode of application. We will then examine the validity of some of its assumptions and show that a major element – that of 'terminal' dates for pigments – is flawed, and needs replacing by a better concept; one describing rates of growth and decline of use. We will also see how this naturally leads to new ways of studying the economic history of pigments. However first, since we are going to use Prussian blue – iron(III) hexacyanoferrate(II) – as a major example, we need some background on its discovery.

The early history of Prussian blue has been extensively recorded and discussed, the best modern account perhaps being that of Harley[2]. The key element to the story concerns a colour-maker, Diesbach, and an alchemist, Dippel, both of whom were recorded as working in Berlin, this story taking place around 1704-7.

*a painting that looks like a Rembrandt can't be by him if it contains the pigment Prussian blue, because that compound wasn't available until well after Rembrandt's lifetime.*

Harley describes what happened as follows: "The chance manufacture of the pigment resulted indirectly from Dippel's production of an animal oil which was distilled over some potash which was then treated as waste. Diesbach, who used to make Florence lake from cochineal, alum, English vitriol [iron(II) sulfate] and a fixed alkali, ran short of alkali and asked Dippel for some of the potash which he saw had been thrown away. He was allowed to use it, and, after he had proceeded by his usual method, the lake appeared to be very pale. When he attempted to concentrate it, it turned purple and then deep blue. Diesbach returned to Dippel for an explanation and was told that the potash was tainted with animal matter."

Manufacturing details of this fortuitous discovery remained secret until they were published in England in *Philosophical Transactions* in 1724, after which time numerous enterprises producing it were set up to satisfy commercial demand. Prussian blue is a good example of what we might loosely call a 'dating' pigment – one with a very clear date of introduction that provides us with a distinct terminal point before which we cannot expect to find it. Thus we may use the presence of this pigment in an object to determine whether it was produced after that key date of discovery (Figure 1).

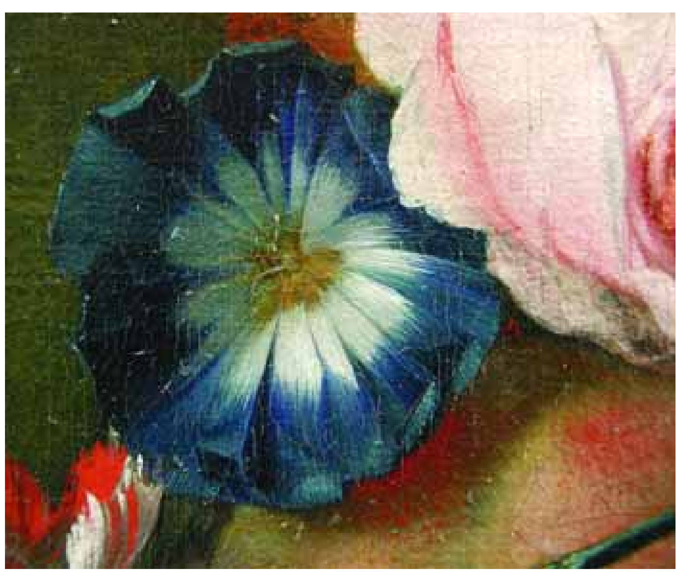

*Fig. 1. A detail of a flower painted using Prussian blue, from an eighteenth century Dutch still-life.*

*much of the basic information comes from standard microscopical techniques that allow us to identify pigments uniquely*

## Methods

It is important to stress before we proceed that studies of this kind must be based on a sound knowledge of the relevant art history, the science involved (mostly the analytical techniques needed, their proper application and interpretation) and a strong grasp of paintings as physical objects, which suffer change and human intervention over time. Without careful reference to each of these it is very easy for the unwary or inexperienced to go astray. It is also vital to take into account other issues, such as historical practices by artists (notably the network of suppliers, assistants, followers, imitators and so forth that have always existed), problems such as sophistication in imitators ('the expert forger' who knows what we know) and a lack of knowledge, where we do not have complete histories of materials. Finally, we have to accept the limitations of our knowledge, where documentary evidence or comparative material simply does not exist. Whatever we do, we must have robust methods that allow us to draw relevant conclusions safely.

Analytically, much of the basic information we use comes from standard microscopical techniques that allow us to identify pigments uniquely – primarily polarised light microscopy, scanning electron microscopy with X-ray spectrometry and Raman microscopy, with others where necessary. From such data we make field-wide, reliable identifications of samples. Earliest and latest identifications of these pigments then give us convenient *terminus ante* and *terminus post* dates for use[3].

In practice, these *terminus ante* and *post* dates can sometimes be well defined, as in the case of Prussian blue, or other products of modern chemistry such as synthetic ultramarine and the various blue and green phthalocyanine compounds, where technological advances led directly to innovative products.

More commonly though, changes in the use of a pigment lie across centuries, or a pigment has been in such constant use historically that its presence seemingly implies no specific time or place. Examples of this might be the almost ubiquitous 'lead white' and the numerous 'earth' pigments – ochres and umbers. Third, there is a group where there is variation, but the rates of introduction and loss are broad, with relatively little currently known about the mechanisms of discovery, dissemination and disappearance; a case in point might be the several lead-based yellow pigments known as 'lead tin yellow', 'Naples yellow', etc.

Consequently we can see that there are situations in which pigments can give us strong, weak or non-existent indications of date. Additionally, similar arguments work for certain painting techniques, combinations of materials used habitually at particular times. A notable example here of a well-dated practice would be the use from roughly the late sixteenth through to the mid-eighteenth century of preparing canvases with two layers before painting – a red one, typically based on a hematite-rich ochre, followed by a grey one, likely to be composed of lead white and charcoal. There are others also.

Such examples imply that there is a certain 'information value' to different pigments and techniques, where something like a synthetic ultramarine would score highly because of its well-known introduction, while undifferentiated ochres or generic lead white pigments would score low. Additionally, when there are multiple indicators present in a work we can be more certain of its date. An example might be the rare combination of Prussian blue with lead tin yellow, the former not originating until the beginning of the eighteenth century, the latter falling largely from use by that time, so that there is a very narrow window within which we might expect to find them together. If we were to extend our 'information value' concept, then complex paintings where there are numerous pigments and techniques, each with their own implications of date, would be preferable to those where there are few, since we have more information on the former on which to judge.

Normal practice when trying to establish a likely date for a painting is to first look for clear examples of anachronism – materials or techniques alien to a specific time or place – and, if there are none, then consider whether the collection of materials and techniques is consistent with the supposed origin. If we find an assembly of pigments often found in the mid-seventeenth century then we might feel more confident in that attribution to Rembrandt than if there were only pigments that could have been used anytime between the 12th and 20th centuries. (Judgements may also be made at this stage about apparently age-related features such as cracks and other degradation phenomena, though these are not very reliable indicators.)

There is a however a common criticism of this last methodology – that many of these historical pigments have continued to be available, (I could in fact go out now and purchase them all from a specialist provider). Hence, these pigments have by implication little or no terminal date and one might consequently argue that we cannot infer anything about dating from pigments post introduction. However, this neglects likelihood – just how often do we expect to find a pigment at any time? Even though a pigment continues to be available, what level of probability is there that we might encounter it in a painting that we might reasonably expect to be 'original'?

## Problems and solutions

More fundamental problems than this actually exist with the idea of 'terminal' dates. While it may sound straightforward to determine the presence or absence of one of these dating pigments and thereby establish boundaries of origin, it is in practice much more difficult than that. One basic problem is how early or late we should actually set these boundaries of occurrence. From our story of the discovery of Prussian blue we have several dates that we could take – the modern reading of the documentary evidence can be no more sure of when the discovery took place than 'sometime between 1704 and 1707. Others have put this latter date at 1710. How then might we deal with a painting of 1706? Or 1708? It could be further argued that although there was pigment production after this time, widespread manufacture probably didn't occur until there was a publicly available recipe in 1724. How then do we

*Normal practice when trying to establish a likely date for a painting is to first look for clear examples of anachronism – materials or techniques alien to a specific time or place*

*This becomes especially important when we are dealing with a painting that may be by the master, but could equally be by a pupil or follower.*

view a painting stylistically thought to be from 1720? This becomes especially important when we are dealing with a painting that may be by the master, but could equally be by a pupil or follower. If the period concerned crosses one of these dating boundaries, then hard evidence on when this boundary falls is crucial. It is surprising how often this is the case!

An alternative approach to this difficulty is to look more closely at the physical record – what do we actually find artists using across that period? Conventionally, we might take all the identified examples of Prussian blue in paintings from that period and use the earliest one as our terminus ante date, then employ it to make decisions about new cases. A better method though is to look at the growth of use – how quickly and how widely Prussian blue was taken up, and then employ that as a measure of relative likelihood – when there is no other evidence to the contrary, is it reasonable to expect to find Prussian blue on this painting at such-and-such a date?

Figure 2 shows data on paintings in which Prussian blue has been identified, taken from a paper reviewing the history and chemistry of the pigment, plotted as a histogram in 50-year bands. There are not really enough cases here, so the distribution is a little rough (it is also quite sensitive to where you place the boundaries; we shall have better examples shortly), but certain trends do begin to appear. There are no examples prior to 1700 of course, but in the earliest band before 1750 there is a huge number that surprisingly, then changes to a slower rise and fall thereafter. Momentarily ignoring the initial peak, the broad rise and fall is in fact typical of use and disuse of pigments and one can plot numerous other examples and find the same unremarkable trend. On the other hand the explanation for the early peak is not hard to fathom. In the period 1700-1750 about a third of the cases come from 1720-25, then the rest in the following 25; this indicates a strong predisposition to identify and report early instances, presumably as these are more 'interesting' and publishable. However, they distort our understanding here and there is a clearly implied need for us as a field to critically evaluate how we collect data for such studies – we should perhaps concentrate less on the major figures of art history and look instead more generally at production of paintings.

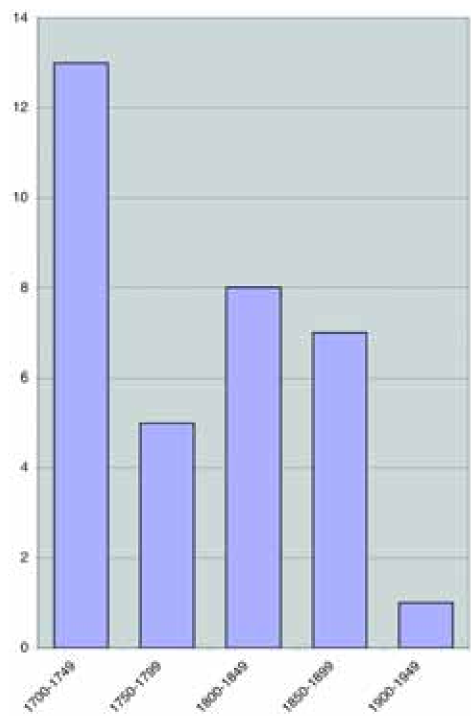


*Fig. 2. Occurrence of Prussian blue in paintings 1700-1950.*

*the logistic model is much more than this, opening up the possibility of studying the underlying mechanisms of pigment use*

In the absence of more reliable data, or worldwide production figures for Prussian blue in the eighteenth century, a more accurate picture probably comes from a similar analysis not of paintings, but published recipes for it. Another recent paper dealing with early Prussian blue[4] details some 100 recipes published up to around

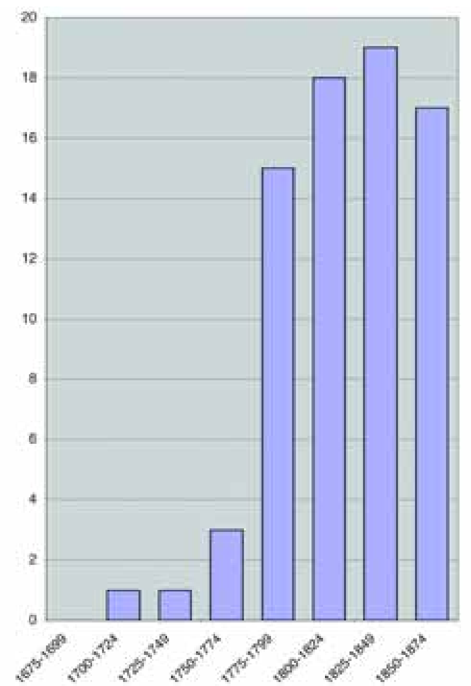


*Fig. 3. Distribution of recipes for Prussian blue, 1700-1900.*

1900. A significant help here is that we have precise dates for them, unlike many paintings. The distribution is much smoother *(Figure 3, in 25-year bands)* and in fact shows the classic form of the so-called 'logistic' differential equation – an induction and exponential rise, then a flattening-off toward some maximal value, the 'carrying capacity'. Such a finding is not surprising: the basic idea of logistic growth is simple and effective, and it is used to this day to model population growth and market penetration of new products and technologies[5].

To reinforce the point that pigment use behaves according to this 'logistic' model we can look at two related pigments: those known as 'lead tin yellow' (a lead tin oxide) and 'Naples yellow' (a lead antimony oxide). Again, data has been drawn from several reviews: Figure 4 shows a logistic fit for lead tin yellow, following data of Martin and Duval[6]; Figure 5 shows data on lead antimony oxide from a review by Wainwright *et al*[7]. In both cases there is a clear relationship, the logistic fit is excellent[8].

We should note though that, particularly with the lead tin oxide, there is probably also a contribution from differences across this period of both production and survival of paintings. In practice, these are also likely to follow a logistic relationship and the graph essentially shows a convolution of the factors. However, for our purposes this is not necessarily a problem, since we are interested in the relative likelihood of finding a pigment from a particular date, a value also dependent on how many paintings there are. This approach is especially useful here since the period of introduction is poorly known; having an estimate of the likelihood of finding this pigment before firm dates of identification is therefore of enormous benefit. It is, incidentally, also possible to model fall of use using negative logistics, though in practice there are better models that describe the entire life cycle of a pigment.

Once we have reached the point of having a convenient and reliable model, then much else falls into place. We can use this model to indicate the likelihood at any time within this phase of a pigment's life cycle of finding it relative to any other. It is also a helpful guide for example where we are reluctant to allow an early date unnecessarily on the sole basis of 'first occurrence'. There has been extensive debate for example, over the introduction of titanium dioxide pigments and whether paintings before, say, 1920 could reasonably contain them. On the basis of this approach such cases would generally be rejected.

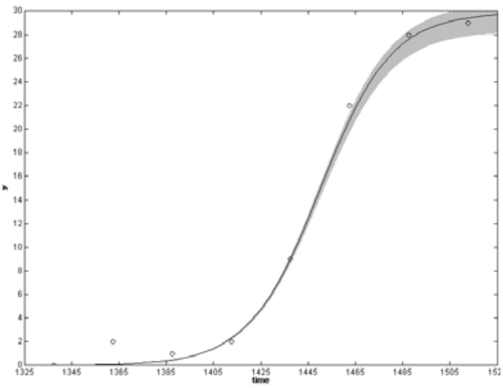


*Fig. 4. Logistic fit of data for occurrence of lead tin oxide in paintings, 1300-1550.*

The model can additionally provide the so-called 'prior knowledge' for more sophisticated approaches to decision-making like Bayesian statistics, a technique that has found widespread use in such allied fields as forensic science but surprisingly not so far in this one.

However the logistic model is much more than this, opening up the possibility of studying the underlying mechanisms of pigment use – how rapidly a historical pigment penetrates a market in

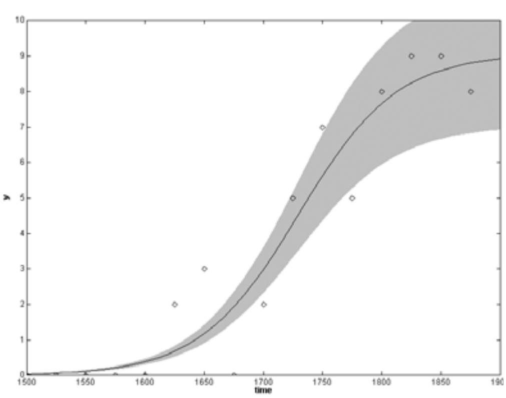


*Fig. 5. Logistic fit of data for occurrence of lead antimony oxide in paintings, 1500-1850.*

different places for example, allowing us to explore the nature of choice and competition.

There are, as always, caveats. In this case a number of factors degrade the quality of the information we have. Broadly speaking these fall into failures of the analysis, unexploited complexities, and inadequacies of reference material. Equally, we can mistakenly identify a pigment, ignore subtleties of composition or structure that provide better information, or have poor information about the true dates of paintings. If we can control these, we improve our techniques. Again, Prussian blue provides good examples of these problems.

Much analysis in this field is still carried out using polarised light microscopy (PLM). An extraordinarily powerful tool for differentiating and identifying historical pigments, its utility cannot be underestimated. However without care, Prussian blue can present problems for secure identification. The main difficulty is differentiation from indigo, a pigment whose importance immediately before the advent of Prussian blue has perhaps been overlooked, and which we now know continued to be used into the nineteenth century, crossing boundaries with Prussian blue.

PLM images of several types of Prussian blue and indigo are shown in Figure 6, and it can be seen that there is a more than passing similarity amongst them. It is therefore understandable that if one does not have independent analytical confirmation of one or the other, and if there is a slight predisposition to underestimate the likelihood of finding indigo in the eighteenth century, then there may well be mistaken identification.

Moreover, some of the simpler confirmatory tests, such as the detection of iron and other elements using micro-chemical tests are not always one hundred percent reliable. Better alternatives are Raman microscopy and microspectrophotometry

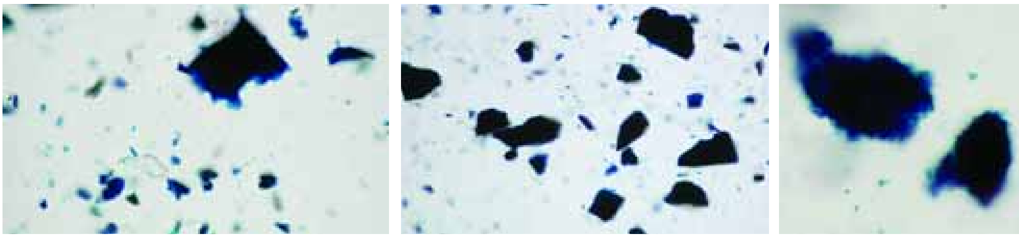

Fig 6a Fig 6b Fig 6c

*Fig. 6. Examples of Prussian blue prepared from blood (a) and pure reagents (Fieldwidth 143 μm) (b), compared with indigo (Fieldwidth 350 μm) (c) (uncalibrated image) (all using polarised light illumination).*

to detect the markedly different transmission of these two pigments in the red/near-IR, are better supplements). Figure 7 shows a typical set-up for combined PLM and micro-spectrophotometry of pigments that might be used for these purposes.

Second, Prussian blue is not really one pigment but several. The chemistry is complex, but we can differentiate so-called 'soluble' and 'insoluble' Prussian blue (a function of the presence of potassium ions inserted into the open cage-like structure of the molecule) and what some refer to as 'early' or 'hand-made' Prussian blue, those products prepared using crude initial ingredients like blood rather than the purer reagents used later. This latter point is of special interest here since all early production must have followed such a route.

Clearly, if we could find a reliable means of differentiating these products (currently we can't), then we could have further characteristics on which to map our date profiles – we should find two logistics, one after the other.

Third, to convert secure identifications into useable probability distributions, we must have independent, accurate dating, of a large group of paintings in which these pigments occur. For this we are heavily reliant on art historical scholarship. Ideally we use signed and dated works only, or at least works where there is very reliable evidence for a particular date, but these can be surprisingly few. A good example occurred in the data used here for developing the histograms – one of the key early examples of Prussian blue cited in the original paper proved, on checking the reliability of the data, to have had its likely date changed; a new diary had turned up since the analysis that showed an assistant to the named artist had in fact finished the painting a decade later! And, of course, we should also be using the techniques I have been describing to check the art history.

Lastly, we must add all those unintended biases, such as the over-reporting mentioned above, or issues to do with the populations from which the examples come (like uneven painting collection practices, or using multiple data from major studies on individual artists).

## Conclusion

Despite scientific analysis of paintings being an area of practical importance, dating has not been subject to the same level of attention as is found in allied fields such as archaeometry or forensics. We have seen though how dating of paintings is currently approached, some specific problems with the methods used, and a potential solution. With the current levels of interest in the physical production of art and its economic contexts, we can expect further development of both robust data and sound theories with which to work. What has been presented here is a simple yet conceptually rich approach that not only provides a sounder foundation for dating works of art, but also of examining the economic mechanisms shaping the creation of each painting.

*Despite scientific analysis of paintings being an area of practical importance, dating has not been subject to the same level of attention as is found in allied fields such as archaeometry or forensics.*

*Fig 7. The author's system for combined PLM and micro-spectrophotometry of pigments. It consists of a Leica DMRX microscope and Ocean Optics S2000 fibre-optic spectrometer with a custom interface.*

**Dr. Nicholas Eastaugh**
The Pigmentum Project,
5 Whitehorse Mews, London SE1 7QD
**neastaugh@pigmentum.org**

Dr. Nicholas Eastaugh is a scientific consultant specialising in the analysis of fine art and other historical objects. He has a background in physics and is also a graduate of the Courtauld Institute of Art. He is currently attached to the Research Laboratory for Archaeology and the History of Art, University of Oxford.

Nicholas Eastaugh is a founder member of the Pigmentum Project, and has recently published the two-volume *Pigment Compendium.*

---

*[1]Radiocarbon dating is rarely applicable because it gives broad multiple date ranges in the modern period unsuited to resolving the quite specific questions often being asked; moreover, sample sizes for paint layers would be unacceptably large. Dendrochronology, though very precise, only helps if the painting is on an oak panel, and even then it dates the support rather than the paint.*

*[2]Harley, R.D. Artists' Pigments c.1600-1835 Butterworth Scientific, London (1982).*
*[3]Kühn. H. "Terminal dates for paintings from pigment analysis" Application of Science in Examination of Works of Art Museum of Fine Arts, Boston (1973) 204.*

*[4] Asai, C. "'Handmade' Berlinerblau" Zeitschrift für Kunsttechnologie und Konservierung 18 (2005) 261-292.*
*[5] The Belgian mathematician Verhulst first introduced this model in the mid-nineteenth century. For a fuller history, see: Cramer, J.S. "The origins and development of the logit model" Logit Models from Economics and Other Fields CUP (2003) Ch. 9.*
*[6] Martin, E.; Duval, A.R. "Les deux variétés de jaune de plomb et d'étain: étude chronologique" Studies in Conservation 35 #3 (1990) 117-136.*

*[7] Wainwright, I.N.M., Taylor, J. & Harley, R.D. "Lead Antimonate Yellow" Artists' Pigments. A Handbook of their History and Characteristics 1 Feller, R.L. (ed.) National Gallery of Art, Washington and Cambridge University Press, Cambridge (1986) 219-254.*
*[8] The data was fitted using the Loglet Lab 2 program; the grey bands indicating the reliability of the fit. See: Meyer, P.S.; Yung, J.W.; Ausubel, J.H. "A Primer on Logistic Growth and Substitution: The Mathematics of the Loglet Lab Software" Technological Forecasting and Social Change 61 (1999) 247-271.*