

# National Gallery Technical Bulletin

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#### FRONT COVER

Titian, *Bacchus and Ariadne* (NG 35), 1520–3 (detail).

#### TITLE PAGE

TOP LEFT: Titian, *The Holy Family with a Shepherd* (NG 4), c.1510 (detail).

TOP RIGHT: Titian, *The Music Lesson* (NG 3), c.1535 (detail).

BOTTOM LEFT: Titian, *Portrait of Gerolamo (?) Barbarigo ('The Man with a Quilted Sleeve')* (NG 1944), c.1510 (detail).

BOTTOM RIGHT: Titian, *'The Aldobrandini Madonna'* (NG 635), c.1532 (detail).

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#### BERGAMO

Comune di Bergamo - Accademia Carrara: fig. 9, p. 9.

#### EDINBURGH

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#### OXFORD

Ashmolean Museum, University of Oxford. Photo: © The National Gallery, London, Courtesy of the Owner: fig. 32, p. 18; figs 37, 38, p. 20; fig. 191, p. 100; fig. 192, p. 101; figs 193, 194, 195, p. 102; figs 196, 197, 198; 199, p. 103; figs 200, 201, 202, 203, 204; p. 104; figs 205, 206, 207, 208, p. 105; fig. 211, p. 107; figs 229, 230, 231, p. 117; figs 232, 233, 234, p. 118; figs 235, 236, 237, 238, 239, p. 119; figs 240, 241, p. 120; fig. 243, p. 121.

#### PADUA

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#### PRAGUE

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#### ST PETERSBURG

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#### VENICE

Gallerie dell'Accademia, Venice © Courtesy of the Ministero per i Beni e le Attività Culturali, Soprintendenza Speciale per il Polo Museale Veneziano: figs 41, 42, p. 23. Photo: © The National Gallery, London, Courtesy of the Owner: fig. 29, p. 17.

#### WARMINSTER

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#### WASHINGTON DC

National Gallery of Art, Washington DC. Photo: © The National Gallery, London, Courtesy of the Owner: fig. 24, p. 14.

## Notes

*Titian's Painting Technique to c.1540*

- 1 For example, the hoax in late eighteenth-century London known as the 'Venetian secret'; see M. Aronson, H.A. Cooper and A. Trumble, 'Benjamin West and the Venetian Secret' in *Spring* 2011, pp. 209–12.
- 2 Lucas and Plesters 1978, pp. 37–47.
- 3 Lazzarini 1983, pp. 135–44.
- 4 For example: Gould 1958; Gould 1961; J. Dunkerton and N. Penny, "'Noli me tangere'", Londra, *The National Gallery* in Rome 1995, pp. 364–7; Penny 1999; J. Dunkerton, 'Titian's Painting Technique' in London 2003, pp. 44–59; Dunkerton and Spring 2003.
- 5 One of the National Gallery paintings, *'The Aldobrandini Madonna'* (CAT. 11, p. 86), was instead examined in 2005 using a Hamamatsu vidicon. Only small areas of particular interest were recorded. *The Triumph of Love* (CAT. 13) was examined using the SIRIS rather than OSIRIS camera.
- 6 Roskill 1968, pp. 184–5.
- 7 Vasari (1568) 1966–87, vol. VI (1987), p. 155. Vasari has the young Titian being placed by his uncle in Giovanni Bellini's workshop.
- 8 C. Hope, 'The Early Biographies of Titian' in Manca 1993, pp. 173ff.
- 9 In the funeral oration for his brother Francesco, who died in 1560, it was stated that both boys went to Venice when Francesco was twelve, but since it is disputed as to who was the elder this is not particularly helpful; see C. Hope in Manca 1993, p. 193, note 79, and Tagliaferro and Aikema 2009, pp. 35–6.
- 10 Hale 2012, p. 45.
- 11 Reproduced in colour in Joannides 2001, p. 11. It is described as 'tempera on panel' but the assumption that a minor painter working in the 1490s would still be working in tempera is not necessarily correct. The landscape, in particular, suggests knowledge of Giovanni Bellini's work. Bellini, and Venetian painters of Zuccato's generation, such as Cima, had been working in oil for most of the last quarter of the fifteenth century; see J. Dunkerton, 'Bellini's Technique' in Humfrey 2004, pp. 198–201, and J. Dunkerton in Conegliano 2010, p. 75.
- 12 For the importance of mosaic in Venice and its effects on the young Titian see Hills 1999, esp. pp. 207–8.
- 13 Joannides 2001, p. 10, and Tagliaferro and Aikema 2009, pp. 282–5. The Zuccato brothers were long-standing friends of Titian and his family.
- 14 Titian's signing of the documents associated with the frescoes of the Scuola del Santo in 1511 as 'Tician depentor' indicates that he was by then a master in the guild. The Venetian painters' guild or *Arte dei Depentori* included painters of all categories, who worked on all types of object. Painters of figures (*depentori de figure*) were of the same status within the guild as painters involved in other crafts, which suggests that when a young painter qualified to practise, the emphasis was mainly on practical aspects of painting. See Rosand 1982, pp. 9–14, and Humfrey 1995, p. 109.
- 15 For the most recent discussion of the Fondaco murals, extensively illustrated, see Joannides 2001, pp. 51–71.
- 16 Colalucci 1991. Titian's fresco technique was very traditional in terms of materials and process, having much in common with trecento frescoes in Padua, such as those of Giusto de' Menabuoi, but the handling is striking for its 'immediatezza ed estemporaneità'. There are no indications of any transfer process for cartoons and instead the first placement of the figures was brushed in with monochrome colours. Some finishing touches 'a secco' survive.
- 17 Colalucci 1991, p. 22. One of the six *giornate* was dedicated just to the raised arm of the woman. *The Miracle of the Speaking Babe* is equally remarkable, with the entire upper part painted in a single day, and the remaining twelve *giornate* given to the figures, either individually or in small groups.
- 18 The fresco of *Saint Christopher* in the Palazzo Ducale, Venice, has only three *giornate*, although the largest of these seems to have been painted over two days. The design was incised directly into the wet plaster, but was not always followed in the painting. See G. Nepi Scire, 'Recent Conservation of Titian's Paintings in Venice' in Venice and Washington 1990, pp. 110–11.
- 19 See Avagnina and Villa 2007, pp. 40–55, for infrared reflectogram details; S. Caglio, F. Frezzato and G. Poldi, 'Pigmenti, leganti, strati: osservazioni analitiche sulla tecnica pittorica del "Battesimo di Cristo"' in Avagnina and Villa 2007, pp. 75–90, for painting materials and layer structure.
- 20 See Hirst and Dunkerton in London 1994, pp. 13–14.
- 21 The *'Gypsy Madonna'* (Kunsthistorisches Museum, Vienna) is the work by Titian most commonly cited as evidence of his debt to Giovanni Bellini, especially as X-radiography and infrared reflectography have demonstrated that it was originally even closer in design to Bellini's *Virgin and Child* in the Detroit Institute of Arts (see E. Oberthaler and E. Walmsley, 'Technical Studies of Painting Methods' in Washington and Vienna 2006, pp. 296–8). Since the painting by Bellini is dated 1509, Titian's work is likely to be later – that is, long after any putative apprenticeship in Bellini's workshop.
- 22 For the Vecellio family see Hale 2012, pp. 9–11.
- 23 It is sometimes assumed that Giorgione's golden yellow draperies are based on orpiment and realgar (see, for example, Washington and Vienna 2006, p. 26), but this is not supported by scientific analysis. While it is possible that small amounts of either pigment might have been used on areas of yellow, these are not the deep orange robes to be seen, for example, on the figure of Saint Peter in Cima's *The Incredulity of Saint Thomas* (NG 816), completed in 1504, and Giovanni Bellini's San Zaccaria Altarpiece of 1505 (Dunkerton and Roy 1986, p. 17, and Lazzarini 1983, p. 139).
- 24 Dunkerton 2010, p. 57; J. Dunkerton, 'Giorgione: "The Adoration of the Kings"' in London 2002, pp. 136–43; E. Oberthaler and E. Walmsley, 'Technical Studies of Painting Methods' in Washington and Vienna 2006, pp. 293–6.
- 25 In 1507 he received a commission for a painting for the Doge's Palace but nothing is known of its subject, size or location. For this and the inaccessibility and confusion about Giorgione's work by the time of Vasari's visits to Venice in the middle of the century see Joannides 2001, pp. 19–25.
- 26 As with so many early works by Titian there are widely divergent opinions on the date of this panel, ranging from 1508 (for example, C. Hope, 'The Early Biographies of Titian' in Manca 1993, pp. 180–2; A. Mazzotta in London 2012, pp. 74–6) to as late as 1514 (for example, Joannides 2001, pp. 166–70; M. Lucco in Rome 2013, p. 57).
- 27 The use of over-heated and heavy irons to attach the new canvas in traditional lining techniques can result in the flattening of the original surface texture and any impasto.
- 28 Matthew 2002, p. 685.
- 29 An entry made in 1600 in the account book of the Verona painter Paolo Farinati (Puppi 1968, p. 167) records the purchase of canvas for a banner with the price *per braccio* and an extra sum for the sewing. This was drawn to our attention by Roland Krischel who has generously shared with us his notes on artists' purchases of canvas in Venice and the Veneto, made, but not used, in connection with his publication of the inventory of the Venetian colour merchant Jacopo de' Benedetti (Krischel 2002 and R. Krischel, 'The Inventory of the Venetian "Vendecolori" Jacopo de' Benedetti: The Non-Pigment Materials' in Kirby, Nash and Cannon 2010, pp. 253–66).
- 30 In their account books, Lorenzo Lotto (Zampetti 1969) and Paolo Farinati (Puppi 1968) regularly record expenses for strainers and tacks together with canvas.
- 31 For other examples and discussion see Dunkerton, Foister and Penny 1999, pp. 266–8.
- 32 Dunkerton and Spring 1998.
- 33 For examples of white layers that could be either a priming or local underpainting in paintings by Bellini see Lazzarini 1983, plate XII; S. Caglio, F. Frezzato and G. Poldi, 'Pigmenti, leganti, strati: osservazioni analitiche sulla tecnica pittorica del

- "Battesimo di Cristo" in Avagnina and Villa 2007, p. 77; Venice 2000, pp. 78 and 82. For Cima see Lazzarini 1983, plate XI; Dunkerton and Roy 1986, pp. 12–13; V. Fassina and F. Frezzato, 'La campagna di analisi sulle tre opere di Cima presente nella diocesi di Vittorio Veneto: studio di materiali pittorici e delle tecniche esecutive' in Spiazzi and Villa 2011, pp. 35–6 (with the observation that *imprimitura* layers are more evident on later works and were not present in samples from the Conegliano Altarpiece of 1493); I. Artemieva and C. Kalinina, 'Sulla storia e sul restauro della pala con "L'Annunciazione" di Giovanni Battista Cima da Conegliano' in Spiazzi and Villa 2011, p. 134.
- 34 Vasari (1568) 1966–87, vol. I (1966), p. 134.
- 35 L. Lazzarini, 'Lo studio stratigrafico della Pala di Castelfranco e di altre opere contemporanee' in Lazzarini et al. 1978, p. 47. The lead white layer occurs in all the samples from the upper part of the painting. The *Laura* (Kunsthistorisches Museum, Vienna) also has gesso and no *imprimitura*. We are grateful to Elke Oberthaler for confirming this point.
- 36 L. Lazzarini, 'Lo studio stratigrafico della Pala di Castelfranco e di altre opere contemporanee' in Lazzarini et al. 1978, pp. 52–6; Lazzarini 1983, plate XIII.
- 37 Laing and Hirst 1986, p. 282.
- 38 Cennini 1960, pp. 19–23. Cennini describes the preparation of lamp black.
- 39 Lomazzo 1584, p. 191. Borghini 1584, pp. 206–7. Armenini (1586) 1988, p. 192.
- 40 Dunkerton and Spring 1998, pp. 128–9, where it was described only as 'fine black' but can now be identified as lamp black.
- 41 Reported as white in Dunkerton and Spring 1998. The presence of lamp black in addition was first reported in Dunkerton and Spring 2003.
- 42 EDX analysis indicated that the zinc was associated with only sulphur in some places, and with both sulphur and potassium in others. The zinc sulphate is perhaps therefore present in two different forms since where potassium was detected the FTIR spectrum was slightly different. In the cross-section from the *Portrait of Gerolamo (?) Barbarigo* (CAT. 5), where associated potassium was detected by EDX analysis, ATR–FTIR micro-spectroscopic imaging gave a sulphate spectrum with a single broad band at c. 1066  $\text{cm}^{-1}$ . In the sample from '*La Schiavona*' (CAT. 6), spectra from a zinc inclusion where no potassium was present gave a more complex sulphate band with a maximum at c. 1040  $\text{cm}^{-1}$  and additional sharp bands at c. 1157 and 966  $\text{cm}^{-1}$ . Zinc soaps were detected in both cases and the spectra suggested that soaps of both the saturated fatty acids and the di-acids may be present. In the sample from '*La Schiavona*', some zinc oxalate was also detected.
- 43 Among them *Sacred and Profane Love* (Galleria Borghese, Rome), probably painted in 1514 (L. Lazzarini, 'Indagini scientifiche sui materiali e la tecnica pittorica dell "Amor Sacro e Profano" di Tiziano' in Rome 1995, pp. 345 and 348–9); probably the Pala Gozzi (Pinacoteca Comunale, Ancona) of 1520 (M. Cordaro, C. Giantomassi and D. Zari, 'Il restauro del dipinto' in Ancona 1988, pp. 39–47, esp. p. 41, and pp. 49–53); the *Portrait of an Elderly Man* (Statens Museum for Kunst, Copenhagen, in Wivel and Filtenborg, forthcoming); *Saint Mark Enthroned* (1511–12) where samples all include, over the gesso, one or two layers of pale grey, interpreted as underlayers but probably a priming, while similar layers are also present on the Pesaro Altarpiece in the Frari, Venice (1519–26), but not on the *Assunta* in the same church, where there is only local underpainting with lead white (L. Lazzarini, 'A Study of Various Works from the Period 1510–1542' in Venice and Washington 1990, pp. 381–3). In the case of the Averoldi Polyptych (church of Santi Nazaro e Celso, Brescia) of 1519–22, preliminary notes without illustrations suggest that a layer of lead white with a little lamp black is present as an *imprimitura* on at least some panels (L. Lazzarini, 'Indagini preliminari di laboratorio' in Lucchesi Ragni and Agosti 1991, pp. 173–7).
- 44 Dubois and Wallert 2003, pp. 23–6.
- 45 For a summary of theories and dates about the execution of this painting see Campbell 2003, pp. 1–7. For the argument for a later date see also Joannides 2001, pp. 151–5.
- 46 Bull and Plesters 1990, where it was published as white. Two samples from this painting, still stored at the National Gallery, were reanalysed. The *imprimitura* is composed of lead white, with a little lamp black, a small amount of dolomite and some yellow iron oxide, the latter two (confirmed by SEM–EDX) most probably both the components of a single earth pigment. This is supported by the analyses of other paintings in this study where yellow earth has been used alone, and where it has therefore been possible to confirm this association. Berrie and Matthew have also re-analysed the *imprimitura* on this painting since the 1990 study, but interpreted the dolomite as a separate addition. See B. Berrie and L. Matthew, 'Lead white from Venice: a whiter shade of pale?' in Spring 2011, pp. 295–301. A similar priming also features on Bellini's *Lady with a Mirror* (Kunsthistorisches Museum, Vienna, information supplied by Elke Oberthaler).
- 47 This is based on recent reanalysis of samples from *The Worship of Venus* and *The Bacchanal of the Andrians* by the scientific laboratory at the Museo Nacional del Prado. We are extremely grateful to Maria Dolores Gayo and Maite Jover for carrying out these analyses and allowing us to refer to them here.
- 48 For the *Assunta* see note 43. For other examples where the only preparation on the canvas is a layer of gesso see Lazzarini 1983; Dunkerton and Spring 1998.
- 49 Dunkerton and Spring 1998. For the advantages of working on coloured grounds and their properties see also Dunkerton, Foister and Penny 1999, pp. 272–4.
- 50 C. Lalli, G. Lanterna, I. Tosini, D. Andrash and F. Innocenti, 'Le analisi del Laboratorio Scientifico dell'Opificio delle Pietre Dure su "La Bella" di Tiziano' in Florence 2011, pp. 89–93.
- 51 Both the painting and the underdrawing on the separated canvas were exhibited, for example, in the exhibition *Le Siècle de Titien* (Paris 1993, p. 157, plate 163). The first recorded discovery of an underdrawing by Titian is surely that of the *Madonna with the Cherries* (Kunsthistorisches Museum, Vienna), revealed during transfer in 1853 and recorded by a painted copy on the back of the original paint film; see Oberthaler and Griesser 2000.
- 52 This underdrawing was presented by Elisabeth Ravaud at a symposium held at CASVA, Washington, DC, in 2006, although the paper has not been published. Two details are reproduced in Washington and Vienna 2006, cat. 31, pp. 168–9.
- 53 For further discussion of transfer techniques for underdrawing in Titian's workshop see Izat 2006.
- 54 Good published examples of characteristic Titian underdrawings in earlier works include the Pala Gozzi (M. Cordaro, C. Giantomassi and D. Zari, 'Il restauro del dipinto' in Ancona 1998, pp. 39–47, esp. p. 41, and pp. 49–53), the '*Gypsy Madonna*' (E. Oberthaler and E. Walmsley, 'Technical Studies of Painting Methods' in Washington and Vienna 2006) and *Jacopo Pesaro being presented by Pope Alexander VI to Saint Peter* (Dubois and Wallert 2003), as well as various other paintings by Titian in R. Bellucci and C. Frosinini, 'Considerazioni sul disegno e "underdrawing" nella pittura veneta e in Tiziano' in Florence 2011, pp. 53–62.
- 55 For good examples of underdrawings by Giovanni Bellini in his late style see E. Oberthaler and E. Walmsley, 'Technical Studies of Painting Methods' in Washington and Vienna 2006, p. 287, and Avagnina and Villa 2007, pp. 40–55; for Cima see J. Dunkerton, 'La tecnica pittorica di Cima' in Conegliano 2010, pp. 70–5; for Giorgione see E. Oberthaler and E. Walmsley, 'Technical Studies of Painting Methods' in Washington and Vienna 2006, pp. 293–6, Dunkerton 2010, p. 57, and J. Dunkerton, 'Giorgione: "The Adoration of the Kings"' in London 2002, pp. 136–43; for Sebastiano see Laing and Hirst 1986, pp. 278–9, although this is not typical as a result of the many revisions. More characteristic fine underdrawing appears on *The Daughter of Herodias* (FIG. 17) and his later Roman paintings; see Dunkerton and Howard 2009, pp. 32–3 and for further references.
- 56 One of the more radical changes of drapery colour in Titian's paintings seems to have been that to the pale lilac (now almost grey) dress of the woman on the left in *Sacred and Profane Love* (Galleria Borghese, Rome). Cross-sections reveal that originally this was a deep red colour, apparently completed with glazes of red lake before the change was made. See L. Lazzarini, 'Indagini scientifiche sui materiali e la tecnica pittorica dell "Amor Sacro e Profano" di Tiziano' in Rome 1995, pp. 347–50.
- 57 R. Krischel, 'The Inventory of the Venetian "Vendecolori" Jacopo

- de' Benedetti: The Non-Pigment Materials' in Kirby, Nash and Cannon 2010, pp. 259–60.
- 58 For the earlier workshops, and especially for Titian's brother Francesco, see Tagliaferro and Aikema 2009, pp. 27–131.
- 59 For example, the series of young women with mirrors from the first decade of the century, probably painted mostly by Titian himself; the different versions of *The Virgin and Child with Saints Stephen, Jerome and Maurice* (W. Deiters, 'Tizian's "Sacre Conversazioni" im Kunsthistorischen Museum, im Chiswick House und im Musée du Louvre' in Vienna and Venice 2008, pp. 141–7); the variations on *'La Bella'* (W. Deiters and N. Gustavson, 'Beispiele der Replizierung von Tizians früheren Bilderfindungen' in Vienna and Venice 2008, pp. 133–40; and also H. Glanville, P. Riitano and C. Seccaroni, "'La Bella" e le Fanciulle di Vienna e Sant Pietroburgo: spunti per una lettura tecnica integrata' in Florence 2011, pp. 63–73). For *'The Aldobrandini Madonna'* derivations see CAT. 11.
- 60 Mills and White 1977, p. 58, and Lucas and Plesters 1978, p. 42.
- 61 Linseed oil was identified in one sample of white paint from *Bacchus and Ariadne* and two samples of brown paint and flesh paint in *Venus and Adonis*. The binder in the later *Vendramin Family* was characterised as walnut oil in six samples from different areas. In addition some GC analysis was carried out in the 1980s on a few samples from *The Feast of the Gods*, in the National Gallery of Art, Washington, DC. See Bull and Plesters 1990, pp. 60–1 and Appendix B, pp. 98–101. Although some of the results were ambiguous due to the presence of later varnishes and retouchings, here too a walnut oil medium was identified.
- 62 No medium analysis has been carried out for *Christ and the Adulteress* (CAT. 2), *Rest on the Flight into Egypt* (CAT. 3) and *'The Aldobrandini Madonna'* (CAT. 11).
- 63 For a more detailed discussion of the preparation of oils, including heat-bodilying, see White and Kirby 1994. In a few samples the ratio of azelate to suberate diacids was a little higher than expected for heat-bodied oil but none of the results obtained gave ratios in the range expected for non heat-bodied oil. This result might also be accounted by a mixture of heat-bodied and non heat-bodied oils; for example, if the pigments were first ground in a non heat-bodied oil (as might be practical since it can be quite difficult to grind them with a rather thick oil), with a proportion of heat-bodied oil then being added on the palette.
- 64 Zinc was also found together with orange and yellow arsenic sulphide in *Jacopo Pesaro being presented by Pope Alexander VI to Saint Peter* (FIG. 27). Dubois and Wallert 2003 (analysis carried out at the National Gallery).
- 65 In Dunkerton and Spring 2003. The inclusions in the priming were analysed only by SEM–EDX and so it was not appreciated at that time that the zinc was present as zinc sulphate, as it has now been possible to show by ATR–FTIR imaging. It was concluded in the earlier study that the zinc was present as part of an earth pigment, as in the sample analysed there was a large yellow-brown agglomerate of iron, copper and zinc compounds. After analysis of more samples, however, this has proved to be anomalous, and is probably an impurity in the zinc vitriol.
- 66 The detection of zinc by XRF analysis has been reported in a significant number of Italian paintings. With this technique, however, it is not possible to determine the form in which the zinc is present. In some analyses a constant iron to zinc ratio was found and it was postulated on this basis that a zinc-rich earth pigment was present. In other cases the correlation with iron was not so certain; it is possible therefore that at least some of these cases represent other examples of zinc sulphate. See Moiola and Seccaroni 2002. See also Borghese, Carini, Olivari and Scatragli 2008, where zinc was reported in *The Adoration of the Kings* by Palma Vecchio, in red areas and those painted with arsenic sulphide pigments; and Amadori et al. 2012, where zinc was found by XRF in paint containing arsenic sulphide pigments. Although again a zinc-rich earth is postulated, it is recognised that it might be present in some other form.
- 67 Similar results were obtained by ATR–FTIR analysis to those for the primings of the *Portrait of Gerolamo (?) Barbarigo* (CAT. 5) and *'La Schiavona'* (CAT. 6), see note 42. Agglomerates containing zinc and sulphur only gave spectra with a complex sulphate band with a maximum at  $c.1040\text{ cm}^{-1}$  and two additional sharp bands at  $c.1157$  and  $966\text{ cm}^{-1}$ . Agglomerates that contained potassium in addition gave a more simple sulphate spectrum with a band at  $c.1070\text{ cm}^{-1}$  and a weak band at  $c.980\text{ cm}^{-1}$ . Zinc soaps, perhaps formed with both saturated fatty acids and di-acids, were also detected by ATR–FTIR.
- 68 See R. Krischel, 'The Inventory of the Venetian "Vendecolori" Jacopo de' Benedetti: The Non-Pigment Materials' in Kirby, Nash and Cannon 2010, pp. 253–66, and L.C. Matthew and B.H. Berrie, "'Memoria de colori che bisognino torre a venetia": Venice as a Centre for the Purchase of Painter's Colours' in Kirby, Nash and Cannon 2010.
- 69 In the fifteenth-century Strasburg manuscript (Borradaile and Borradaile 1966), for example, 'galicen stein' is an ingredient in a recipe for preparation of an oil that will make it 'much clearer and paler' as well as 'very quick drying', and it is also suggested that a small quantity 'as much as a bean' can be mixed with colours on the grinding slab 'in order to make the colour dry well' (Borradaile and Borradaile 1966, pp. 54–5). Charles Lock Eastlake discussed zinc vitriol as a drier at length and believed it was the favourite siccativ of the Northern European painters of the fifteenth century; see Eastlake 1847 (1960), pp. 130–1. He interpreted 'galicen stein' as zinc vitriol, white copperas, and it is certainly a zinc compound. Zinc ions are a so-called secondary drier. They increase the effectiveness of a primary drier (one which accelerates the drying of the paint surface) and encourage through drying of the paint film below the surface; see Tumosa and Mecklenburg 2005, and Erich 2006, pp. 10–12, for a summary of the action of driers.
- 70 The recipe (no. 339) is entitled 'Mordant for gilding glass, which has been tried by a Venetian Friar' (Merrifield 1849, vol. 1, p. 620). Mary Philadelphia Merrifield in her English translation lists 'coperosa, which must be fine and white and not grey' as one of the ingredients in this oil-based mordant or adhesive. As it is described as white this is clearly zinc vitriol (zinc sulphate) rather than another type. A recent Italian annotated edition of the Marciana manuscript dates it to the second half of the sixteenth century and transcribes this material as 'coperosa che sia bella et bianca': see Frezzato and Seccaroni 2010, p. 155 (entry 339).
- 71 Zinc sulphate has been found in Stephan Lochner's *Saints Matthew, Catherine of Alexandria and John the Evangelist* (NG 705), about 1450, and in the Master of Liesborn's *The Adoration of the Kings* (NG 258). In these works, however, it is always in paint composed of red lake, and since recipes for this pigment exist that include zinc vitriol it may be that here it is not associated with the medium, and is not a separate additive. Two other examples are Jan van Eyck's *Arnolfini Portrait* (NG 186) and his *Portrait of Margareta van Eyck* (Groeningemuseum, Bruges). For more details on these paintings and on the recipes see Spring et al. 2012; Spring and Morrison, forthcoming. The presence of zinc (but not confirmed as zinc sulphate) has also been reported in a number of other paintings by Lochner and other Cologne painters; see Stege et al. 2012.
- 72 An example in red lake paint in what is probably an early work by Garofalo from around 1500 is published in Kirby, Spring and Higgitt 2005. It has also been detected in red paint in a large altarpiece by Lorenzo Costa and Gianfrancesco Maineri, from around 1500 (NG 1119), and two works by Giovanni Battista da Faenza from 1500–15 (NG 282 and NG 1051). In the second of these it was possible to show that the zinc is present as zinc sulphate by ATR–FTIR imaging, in a pale pink underlayer for a red lake layer. It was also found in this work together with arsenic sulphide pigments in orange paint. Other examples of zinc in orange and yellow areas painted with orpiment or realgar (revealed by XRF) have been reported in paintings by Palma Vecchio (see Borghese, Carini, Olivari and Scatragli 2008).
- 73 See the examples in note 72, many of which are earlier in date than the paintings by Titian and are from elsewhere in Italy.
- 74 Merrifield 1849, vol. I, p. cli. See also Krischel 2002, p. 128; B. Berrie and L. Matthew, 'Lead white from Venice: a whiter shade of pale?' in Spring 2011, pp. 295–301; M. Stols-Witlox, "'The heaviest and the whitest": lead white quality in north western European documentary sources, 1400–1900' in Spring 2011, pp. 284–94.
- 75 B. Berrie and L. Matthew, 'Lead white from Venice: a whiter shade of pale?' in Spring 2011, pp. 295–301. Stols-Witlox, Megens and Carlyle 2012.

- 76 See Gettens, Kühn and Chase 1993, pp. 75–6. Both types were confirmed by FTIR in the white drapery in *The Music Lesson* (CAT. 12), in sky paint in *Noli me Tangere* (CAT. 7) and in the grey background in the *Portrait of Gerolamo (?) Barbarigo* (CAT. 5).
- 77 Stols-Witlox, Megens and Carlyle 2012, Boon and Oberthaler 2010.
- 78 See Krischel 2002. The earliest document that mentions a *vendecolore* in Venice is from 1493, where this seems to have developed as a specialist profession earlier than in other cities; see L.C. Matthew and B.H. Berrie, “Memoria de colori che bisognino torre a vinitia”: Venice as a Centre for the Purchase of Painter's Colours’ in Kirby, Nash and Cannon 2010.
- 79 Matthew 2002.
- 80 The exception is *The Music Lesson* (CAT. 12), but only one figure is wearing blue, the man with the green hat in the background, part of whose dark blue sleeve is just visible beside the viol. The music masters's cloak, although it appears blue, is in fact azurite mixed with some red lake, so was intended to be purple or purple-blue rather than a pure blue.
- 81 When ultramarine pigment in paint samples is analysed, at least some colourless minerals associated with the lazurite are always found, but in the paintings in this study the proportion of these seems to be particularly low. Some recent studies have attempted to characterise the different grades that are produced by the traditional extraction process based on the associated colourless minerals, since these are preferentially removed at the different stages depending on their physical and chemical processes; see Favaro et al. 2012. In these paintings by Titian there is some indication that the stone itself was of particularly high quality, since pyrite is present even though it has been shown that this is usually among the minerals removed during the first extraction.
- 82 Kirby 2000, pp. 19–42.
- 83 Lazzarini 1983, where smalt is reported in the *Pala Pesaro*, but as a small component in the ultramarine paint and identified only by optical microscopy, which may not be reliable.
- 84 This has been suggested for the ultramarine blue drapery of the nymph carrying an urn in Giovanni Bellini's *The Feast of the Gods*, which has a pink underpaint; see Lucas and Plesters 1978. Other examples include works produced in Rome by Sebastiano del Piombo; see Dunkerton and Howard 2009, pp. 36–7.
- 85 Spring 2012.
- 86 A. Burmester and C. Krekel, “Azzurri ultramarini, lacche et altri colori fini”: The quest for lost colours’ in Munich 2000, pp. 193–212.
- 87 Cardon 2007.
- 88 Monnas 2012, p. 23.
- 89 Kirby, Saunders and Spring 2006, and Cardon 2007, pp. 614–16 and 642–6.
- 90 Indeed, red fibres that have become incorporated into the pigment are sometimes found on paintings. See Kirby, Spring and Higgitt 2005.
- 91 A madder lake with similar characteristics was also identified, again in addition to kermes, in *Jacopo Pesaro being presented by Pope Alexander VI to Saint Peter* (FIG. 27). Dubois and Wallert 2003, p. 36.
- 92 Madder lakes in other paintings have often been found to contain protein, resulting from the dyestuff having been extracted from wool shearings; see Spring et al. 2012, and Kirby, Spring and Higgitt 2005. There was no evidence of this in the paintings in this study; this does not necessarily mean that wool shearings were not used as a dyestuff source – madder would not have been used to dye silk and it is unlikely that the dyestuff was extracted direct from the root – but simply that a recipe was used that did not dissolve the wool fibres. Silk fibres are less soluble, and it is easier to extract the dyestuff, so the protein from silk does not make its way into the pigment. The presence in one sample from a painting in this study of a trace of ellagic acid, used to weight silk, indicated that at least one of the red lakes had been prepared by extracting the dye from the shearings of a silk textile.
- 93 See Kirby, Saunders and Spring 2006.
- 94 HPLC analysis identified kermes from the scale insect *Kermes vermilio* Planchon with smaller quantities of carminic acid (derived from cochineal), and traces of components that perhaps relate to lac in *The Vendramin Family* (NG 4452).
- 95 The red lake from *The Death of Actaeon* (NG 6420) contained only carminic acid, indicating a variety of cochineal, although it was not possible in this case to distinguish New World cochineal from the Old World Armenian variety analytically. It seems likely, however, based on the dates, that New World cochineal from *Dactylopius coccus* Costa was used both here and in *The Vendramin Family* (see note 94). See also note 97.
- 96 J. Plesters and L. Lazzarini, ‘I Materiali e la Tecnica dei Tintoretto della Scuola di San Rocco’ in Rossi and Puppi 1996, pp. 275–80; Kirby and White 1996, p. 71. The red lake in Veronese's *The Adoration of the Kings* (NG 268), previously published as Polish cochineal, has been reanalysed and it now seems more likely that this pigment is cochineal of the New World type. Therefore it would be worth reconsidering the result from Veronese's *The Consecration of Saint Nicholas* (NG 26), which was published as probably Polish cochineal. One painting by Tintoretto, *The Origin of the Milky Way* (NG 1313), was found to contain lac. But overwhelmingly the existing red lake analyses from Venetian pictures in the later sixteenth century have identified carminic acid.
- 97 The identification of Polish cochineal from *Porphyrophora polonica* Linnaeus and similar species is based on the detection of carminic acid with up to 15% kermesic acid and flavokermesic acid in addition. This can therefore be difficult to distinguish if a mixture of kermes and a carminic acid-containing dye are present. However, the absence of a significant amount of kermesic or flavokermesic acid generally indicates that the dyestuff is not of the Polish cochineal type. The distinction between the Old World Armenian variety from *Porphyrophora hamelii* Brandt and related species, and the New World cochineal from *Dactylopius coccus* Costa, is even more difficult to make. These two dyestuffs differ only in the proportions of the minor components, particularly that known as dClI. However, in practice dClI is rarely detected by HPLC analysis in samples of red lake paint, so it is generally not possible to specify analytically whether the source of the carminic acid is the New World or Old World Armenian variety. See Cardon 2007, chapter 12.
- 98 This could be due to the relative expense of the Old World cochineal dyestuffs which were reserved for dyeing only the most expensive types of cloth, perhaps making shearings from these textiles less available to the pigment industry (see Molà 2000, pp. 107–31). One example of a pigment of this type is the red lake from the robe of the kneeling figure in *The Adoration of the Kings* attributed to the workshop of Giovanni Bellini (NG 3098), dated to about 1475–80. HPLC analysis identified carminic acid with some kermesic acid and the source of the dyestuff is likely to be Polish cochineal; Kirby, Spring and Higgitt 2005, p. 86.
- 99 For a discussion of names used for yellow lead-containing pigments see Kühn 1993 and Seccaroni 2006.
- 100 This will depend on whether yellow lead oxide (litharge, PbO) or red lead is used as the starting material. Both of these compounds react more readily with the binding medium to form lead soaps than lead-tin oxide, which might explain why this has happened so extensively in Titian's paints, but since these oxides have been converted to soaps it is no longer possible to determine the starting material in this case, and whether the lead-tin yellow was originally more golden, as would be the case if unreacted red lead was present, or a rather pale variety, as it would be if unreacted litharge was present. Litharge associated with lead-tin yellow has been found by Raman analysis in paintings by Lotto, where it was, as here, interpreted as resulting from the preparation procedure of the lead-tin yellow; see Amadori et al. 2012, p. 19. Experiments making yellow lead-containing pigments to different recipes can be found in Pelosi et al. 2010.
- 101 Fitzhugh 1997, pp. 49–50. Hills 1999, pp. 146–50.
- 102 Fitzhugh 1997, pp. 49–50. Garofalo also used orpiment and realgar sparingly in this way; see Dunkerton, Penny and Spring 2002.
- 103 We are grateful to Janet Ambers at the British Museum for the Raman microspectroscopy, which was carried out with a 785 nm laser, using powers of less than 0.5 mW at the sample to avoid thermal degradation.
- 104 See Corbeil and Helwig 1995. The characterisation of arsenic sulphide pigments is complex, since it seems that both mineral and artificial varieties might have been used, with evidence of the latter being imported into Venice from Germany or Austria at this time (see G. Grundmann, N. Ivleva, M. Richter, H. Stege

and C. Haisch, 'The rediscovery of sublimed arsenic sulphide pigments in painting and polychromy: applications of Raman microspectroscopy' in *Spring* 2011, pp. 269–76. Burnt orpiment which was orange is also mentioned in documentary sources as a pigment.

- 105 Although it is possible that dolomite (calcium magnesium carbonate) has been added as a colourless extender, it is consistently present together with yellow iron oxide, so it seems most likely to be associated with the earth pigment. Some dolomite was also found with azurite in blue layers; it is common to find it associated with this particular blue mineral. Lazzarini mentions that, in Venice, earth pigments might have been obtained from the mainland: for example, 'terra gialla di Verona', which he says is from the area between the Avesa and the Valpantena valleys (although he states that it has a high limonite content of 50–60%, which does not match that found in the Titian paintings). See Lazzarini 1987, p. 118.
- 106 On this point see, in particular, Hills 1999, pp. 173–85.
- 107 M. Griesser and N. Gustavson, 'Beobachtungen zu technik und Material in Tizians Spätwerk' in *Vienna and Venice 2008*, pp. 101–10.

### Cat. 1 *The Flight into Egypt*

- 1 The painting was cleaned and restored by Valery Shatsky and Alexander Kuznetsov in the Laboratory for the Restoration of Oil Paintings of The State Hermitage Museum. The cleaning involved the removal of thick layers of very discoloured varnish and large amounts of repainting.
- 2 For a full account of the painting's history and discoveries made during the treatment, see Artemieva 2012, pp. 4–11.
- 3 Artemieva 2012, p. 10.
- 4 This point was made by Jennifer Fletcher at a seminar on 23 June 2012 in association with the exhibition *Titian's First Masterpiece*. For the Ca' Loredan, including extracts from Andrea di Nicolò's will mentioning his paintings, tapestries and sculpture, which he wished to remain in the palace, see Olivato Puppi and Puppi 1977, pp. 221–3.
- 5 Artemieva 2012, p. 11. For the canvas of *The Judgement of Solomon* see Laing and Hirst 1986, p. 282. Since the selvages have survived along the seam it has been possible to establish a canvas width of about 78 cm.
- 6 Laing and Hirst 1986, pp. 274–81.
- 7 Their poses are very similar to those in the tiny panel of the *Holy Family in a Landscape* in the North Carolina Museum of Art, Raleigh, which is widely accepted as one of Titian's earliest works; a larger version is in St Petersburg.
- 8 Joannides 2001, p. 39, proposes that the subject is best described as the 'Thanksgiving on safe deliverance to Egypt'.
- 9 Artemieva 2012, p. 7.
- 10 SEM–EDX analysis also revealed the presence of a significant amount of sulphur in addition to carbon, confirming that the pigment is coal black.
- 11 See essay, pp. 24–5, and the entries for *Portrait of Gerolamo (?) Barbarigo* (CAT. 5, p. 54), *Portrait of a Lady ('La Schiavona')* (CAT. 6, p. 61) and the Glasgow *Christ and the Adulteress* (CAT. 2, p. 41).
- 12 SEM–EDX analysis of the large red lake particle at the left, which is probably madder lake, based on its orange fluorescence under ultraviolet light, showed a strong peak for aluminium and a smaller peak for sulphur, with minor amounts of other elements. This is very similar to the madder lake in *The Holy Family with a Shepherd* (see CAT. 4, p. 49).
- 13 SEM–EDX analysis indicated that the earth pigment is rich in silicates and also includes a mineral component containing calcium and magnesium which is probably dolomite, as well as a small amount of a black<sub>3</sub> mineral containing iron and titanium, probably ilmenite (FeTiO<sub>3</sub>). This was also found as an impurity in the earth pigment used in *Bacchus and Ariadne* (CAT. 8, note 20).
- 14 The binding medium was analysed by GC–MS in samples from green grass, Joseph's yellow cloak and the Virgin's red dress. The azelate/palmitate ratio ranged from 0.8 to 1.4, while the palmitate/stearate ratio ranged from 1.0 to 1.9.

### Cat. 2 *Christ and the Adulteress and Head of a Man*

- 1 The painting was cleaned and restored at the National Gallery; an account of the treatment appears in Ruhemann 1955, pp. 278–82. His description of the technique (characteristic in its emphasis on the apparent use of monochrome undermodelling) is not supported by the evidence of the paint cross-sections. The painting was sampled by Joyce Plesters at the time of the cleaning and then again by Joyce Plesters and Ashok Roy in 1980 when both fragments were exhibited at Wildenstein's. The painting is badly abraded from past cleaning, notably in the foreground, in the background above Christ, the torso of the old man next to Christ, the area between the young man and the Adulteress and the robes of the figure behind her. There has been flaking along the join, particularly across Christ and the soldier to the left. Other areas are affected by drying cracks that have developed as a result of defective technique and the numerous pentimenti.
- 2 For a full account of the history of attribution and discussion of the subject of the painting see Humfrey 2012, pp. 90–6.
- 3 Humfrey 2012, pp. 95–6.
- 4 The choice of a canvas of this width would also have saved wastage with a painting of these dimensions. If a wider loom width had been used a strip would need to be trimmed off or alternatively two pieces joined with the warp perpendicular to the main piece, a technique often seen in Venetian canvases.
- 5 In Humfrey 2012, pp. 94–5. They were made by Giovanni C.F. Villa when the painting was on display in Edinburgh.
- 6 The painting was X-rayed at the National Gallery during the cleaning in 1951–3. Unfortunately the individual X-ray plates did not overlap and so it is not possible to assemble them into a full mosaic. An attempt was made for Humfrey 2012, fig. 3, p. 94, but it appears that the positive films (used to make prints from the original X-rays) were used and so the image is inverted, with areas that absorb X-rays appearing dark instead of light. The images reproduced here are from a set of prints from the positives held in the Photographic Library at the National Gallery.
- 7 Humfrey 2012, p. 93.
- 8 SEM–EDX analysis and ATR–FTIR microspectroscopic imaging on the cross-section identified zinc sulphate and zinc soaps. The FTIR spectra suggest that a combination of soaps of both the saturated fatty acids, palmitate and stearate, and the diacids, such as azelate, may be present. Some of the inclusions were found by SEM–EDX analysis to also contain a small amount of potassium and gave a slightly different FTIR spectrum. See essay, pp. 24–5, for a more detailed discussion and for other paintings in this study where zinc sulphate and zinc soaps were found. The only pigment in the red layer is vermilion. The brown layer contains earth pigments, including some with a manganese content, as well as some calcium carbonate which may be a component of the earth pigment, a little lead-tin yellow, lead white and black.
- 9 HPLC analysis identified the dyestuff as kermes from the scale insect *Kermes vermilio* Planchon. Kermes has also been found to be the major dyestuff in samples of red lake from *The Holy Family* (CAT. 4), *'La Schiavona'* (CAT. 6), *Noli me Tangere* (CAT. 7) and *The Music Lesson* (CAT. 12). A small peak for alizarin was also detected but the other components expected for madder were not observed and it seems likely that it represents a modern retouching. This would be consistent with the appearance of the cross-section sample under ultraviolet light, as there seems to be a thin additional layer at the surface that is separated by a fluorescent varnish layer.
- 10 See entry on *Bacchus and Ariadne* (CAT. 8, p. 73).
- 11 Confirmed by SEM–EDX analysis.
- 12 The dress of Profane Love, on the left in *Sacred and Profane Love* (Galleria Borghese, Rome), now appears almost white, shaded with grey, but paint samples indicate that a small amount of red lake was included in the paint mixture. See L. Lazzarini, 'Indagini scientifiche sui materiali e la tecnica pittorica dell' "Amor Sacro e Profano" di Tiziano' in *Rome 1995*, p. 347.
- 13 See Dunkerton and Roy 1986, pp. 15–16, and note 34, p. 26. They have also been observed in samples from Venetian works by Sebastiano del Piombo; see Lazzarini et al. 1978, p. 54.
- 14 Humfrey 2012, p. 93. This information derived from a letter by Joyce Plesters to Jaynie Anderson. See Anderson 1997, p. 327.

The samples are still kept at the National Gallery and were re-analysed by SEM–EDX, showing that the orange areas are a mixture of lead-tin yellow, red earth and a little vermilion, while the yellow highlights contain only lead-tin yellow.

### Cat. 3 *Rest on the Flight into Egypt*

- 1 Mazzotta 2012, p. 77, dates it to 1508–10. Joannides 2001, p. 161, prefers the later date of 1512, and Wethey 1969–75, vol. II, p. 125, the even later date of 1515.
- 2 Infrared reflectography was carried out at the National Gallery on 13 March 2012 with the same equipment used to examine the National Gallery's own paintings.
- 3 Presented by Troels Filtenborg at a seminar held at the Statens Museum for Kunst, 6 March 2012. See also Wivel and Filtenborg, forthcoming; we are grateful to the authors for sharing their results before publication.
- 4 Reproduced in Joannides 2001, fig. 142, p. 161. The painting was auctioned in Milan in 1995 as a work by Titian. If so, it is likely to have been heavily repainted and it may well be a later production, perhaps of the seventeenth century (private communication from Antonio Mazzotta).

### Cat. 4 *The Holy Family with a Shepherd*

- 1 The painting is generally well preserved. There are scattered losses, mainly from the sky and Saint Joseph's cloak, and some of the more thinly painted areas are slightly abraded, showing the tops of the canvas threads. The worst affected area is the landscape between the Christ Child and Joseph. The varnish layers applied in the last restoration are now slightly discoloured and have lost some transparency, particularly over the ultramarine blue of the Virgin's mantle.
- 2 Joannides 2001, p. 145.
- 3 Gould 1975, p. 267–8.
- 4 In the X-ray images of the bottom left corner of the picture the bottom edge of the original canvas looks as though it is a selvedge.
- 5 This is supported by the presence of an orange layer consisting of a mixture of lead-tin yellow, lead white and red earth (identified by EDX), in one of the cross-sections taken in 1953, beneath the layers that make up the orange cloak as finally painted.
- 6 These paint samples were first published and discussed in Dunkerton and Spring 2003, pp. 16–21.
- 7 These particles have the appearance of charcoal, but this has not necessarily been used in the form of a dry drawing medium, since the appearance of the lines in infrared images suggests that the drawing medium was wet. In cross-sections the medium around the particles is not visible, but this is not unusual even where the underdrawing is wet, and could also be a consequence of drawing with a very dry brush.
- 8 The pigment can be seen in a cross-section to still have a strong blue colour while, as is often observed in bleached ultramarine-containing paint, the matrix around it appears cloudy and there is a greyish crust on the surface. The problem might also be exacerbated by the deterioration of the varnish layers applied in 1953.
- 9 Lazzarini 1983. Apart from the occurrences on Titian's *Assumption of the Virgin* of 1518 and the Pesaro Altarpiece of 1519–26, where in both cases the indigo is mixed with lead white as a first lay-in for areas of blue (see p. 142 – the term *imprimitura* is here used in the sense of a local underpainting), the only other painting with indigo listed in Lazzarini's extensive table is by Tintoretto. See discussion in the essay, p. 27.
- 10 HPLC analysis identified kermes from the scale insect *Kermes vermilio* Planchon. Smaller quantities of methylated pseudopurpurin and purpurin were also present, indicating the presence of a pseudopurpurin-rich madder, presumably from *Rubia tinctorum* L. No alizarin was detected but this is often only a minor component of madder lakes at this date. EDX analysis of the substrate of the red lake in the upper layers, the kermes lake, found some alum (potassium aluminium sulphate) dispersed in the layers, and spot spectra of individual large lake particles

indicated that some potassium was incorporated in the hydrated alumina substrate. Alum is a starting material used in lake making, but usually an alkali is added to the dye solution so that alumina, which has formed a salt with the dyestuff, precipitates from the solution. In this case it appears that the precipitation has not gone to completion. The madder lake substrate appeared to be slightly different, with almost no potassium incorporated in the alumina substrate.

- 11 Realgar and pararealgar were identified by Raman microscopy. We are grateful to Janet Ambers at the British Museum for this analysis. The pararealgar, which is yellow, is likely to be a degradation product (see essay, p. 30). Zinc was detected by EDX analysis on a cross-section from Joseph's orange mantle in the realgar layer. It does not appear to be associated with iron, and is probably not therefore present as a zinc-rich earth pigment. Although in '*La Schiavona*' (CAT. 6, p. 61) and *Portrait of Gerolamo (?) Barbarigo* (CAT. 5, p. 54) it was confirmed that the zinc is present as zinc soaps and zinc sulphate, this was not possible in these samples as too little was present.
- 12 For the emergence of orange colours as distinct from yellow, and especially in Cima's paintings, see Hills 1999, pp. 146–50. Arsenic-based pigments have recently been found on Cima's earliest altarpieces dating from the late 1480s and early 1490s, including the Olera, Vicenza and Conegliano altarpieces; see G. Poldi, 'L'arancio e altri gialli. Spigolature sui pigmenti di Cima a fronte di trentuno opera esaminate' in Spiazzi and Villa 2011, pp. 43–55. For the layer structure of Saint Peter's orange robe in *The Incredulity of Saint Thomas* (NG 816) see Dunkerton and Roy 1986, p. 13.
- 13 The actual execution of this altarpiece is often dated to late in the decade, but for the argument that it may have been painted as early as 1505 see Conegliano 2010, p. 204.
- 14 Only a small amount of chloride was detected by EDX analysis, suggesting that it is a secondary product from a traditional method of manufacture of verdigris, in which copper plates coated in honey and common salt are exposed to acetic acid vapour; see Kühn 1990, where examples of copper chloride-containing verdigris in paintings are reported, together with a discussion of relevant recipes in treatises.
- 15 The identification of these glazes demands a refined means of analysis and thus few other examples have been reported to date. However, at the National Gallery they have now been found on a number of fifteenth- and sixteenth-century paintings by, among others, Uccello, Raphael, Garofalo and, perhaps most significantly for Titian, Cima da Conegliano.
- 16 These medium analysis results were reported in Dunkerton and Spring 2003. It was suggested that in the red lake glaze of the Virgin's drapery the heat-bodied linseed oil was combined with a little pine resin. Pine resin may have been added to increase the transparency and gloss of this glaze but it should be noted that this result could also be due to a small amount of varnish contamination. In the subsequent analyses of other paintings undertaken in this study, traces of resin including pine resin have been detected but these have normally been linked to the materials in the varnish layers and no definite evidence of resinous additions to Titian's media has been found.

### Cat. 5 *Portrait of Gerolamo (?) Barbarigo ('The Man with a Quilted Sleeve')*

- 1 The varnish layers applied in the restoration are now slightly discoloured and opaque and some retouchings have altered. The condition of much of the paint surface is reasonably good, although there is evidence of abrasion in the black cloak and on the face, particularly at the junction of cheek and beard. In the lower corners there are extensive losses from flaking, now much retouched. On the right side the area affected extends into the lower sleeve and hand. The old, but non-original, inscription 'TITIANUS' was retained but has been touched out.
- 2 Mazzotta 2012, pp. 12–19.
- 3 Vasari (1568) 1966–87, vol. VI (1987), p. 156.
- 4 Medium analysis was carried out by GC–MS.

- 5 SEM–EDX analysis confirmed the presence of zinc and sulphur in the inclusions, with some potassium in addition in some areas. Analysis by ATR–FTIR microspectroscopic imaging showed that the zinc was present in the form of sulphates and soaps. The FTIR spectra suggest that a mixture of zinc soaps may be present including those of the saturated fatty acids, palmitate and stearate, and the diacids, such as azelate.
- 6 Medium analysis was carried out by GC–MS on samples taken from the edges. It is worth noting that no samples were taken for medium analysis from the lighter passages of paint; the flesh or the white *camicia*, for example.
- 7 The deepest blue areas, on his chest, where the paint contains rather little lead white are also slightly blanched, a deterioration most probably associated with the ultramarine pigment.
- 8 Vasari (1568) 1966–87, vol. VI (1987), p. 156.
- 9 During the cleaning of 1949, overpainting of the beard and hairline, including coarsely painted strokes of hair, was removed. This repaint (well documented by photography) dissolved off with the varnish and was clearly relatively recent. See National Gallery Conservation Record, p. 12.

#### Cat. 6 *Portrait of a Lady* ('*La Schiavona*')

- 1 There are many small losses from the paint and ground that appear to have been the result of rolling of the canvas for transport in the past. There are also filled losses on the woman's face that appear to be related to wide drying cracks. The paint of the background is much abraded and has been extensively retouched. The oculus to be seen in FIG. 110 was retouched, together with the rest of the painting, before photography on 8 September 1960. The oculus was then painted out and the painting re-photographed on 3 March 1961.
- 2 See N. Penny in London 2003, p. 80, for discussion of the identity of the woman.
- 3 See Gould 1961, pp. 334–40, for an account of the discoveries made during cleaning.
- 4 In Gould 1961 some doubt is expressed as to the sequence of these changes in the background. Re-examination of the 1961 samples confirmed that immediately below the lower edge of the rectangle there is grey paint directly on the priming, beneath the paint associated with the sky and landscape seen through the circular porthole, confirming that the rectangle was the first idea and that the grey background had already been blocked in around it.
- 5 Joyce Plesters stated in her 1960 report on examination of samples that this dark grey paint showed 'a remarkable resemblance to the original dark grey paint on the rest of the background' based on the observation that they both contained a similar fine-grained black pigment mixed with lead white, some particles of the latter being quite large. She concluded that it was 'very likely but not certain' that the roundel window was covered up by the artist himself. New SEM–EDX analyses on the surviving 1960 cross-sections have shown that the dark grey paint contains in addition the same dolomite-containing earth pigment as the rest of the background. It would seem to be almost impossible that a later restorer would use this same mixture and we can therefore now be more certain that it was indeed Titian who painted out the roundel.
- 6 See N. Penny in London 2003, p. 80.
- 7 Summarised by N. Penny in London 2003, p. 80.
- 8 For the possible meaning of the initials see N. Penny in London 2003, p. 80.
- 9 Identified by SEM–EDX analysis and ATR–FTIR microspectroscopic imaging on a cross-section. As in CATS 2 and 5 (pp. 41 and 54) a small amount of potassium was detected in addition suggesting more than one type of sulphate might be present. Zinc oxalate, probably a degradation product, was also identified.
- 10 Medium analysis was performed on samples from the edges of the painting. A portion of each was first analysed by GC–MS, but in several of the samples interpretation of the analysis was complicated by the presence of beeswax as a contaminant, probably from conservation treatment. The remainder of the sample was rinsed with xylene then methanol to remove the beeswax contamination and again analysed by GC–MS, which gave more secure results.
- 11 Previously described by Dunkerton and Spring 2003, pp. 18–19. The samples were re-examined and analysed further during the present study, as were those taken during the 1961 restoration, most of which still survive in reasonably good condition.
- 12 This probably represents overlapping strokes from the same undermodelling rather than a separate stage. Some indigotin was detected by HPLC when a sample was taken from the upper purple and red layers for identification of the dyestuff in the red lake pigment (see note 14). It is unlikely to be in these upper layers. Instead, the sample probably included a little of the blue undermodelling. Although indigo was not initially observed by optical microscopy in cross-sections, in one sample where the layer is a darker blue, the lead white matrix (between easily visible particles of ultramarine) does appear 'stained' blue, as it might be if it contained indigo, which is of extremely small particle size.
- 13 The same method described in note 10 was used, since again the samples were contaminated with beeswax. The light pink underlayer was exposed at the left edge where the painting is usually covered by the frame so that it was possible to sample it separately. No samples could be taken from either the white passages of drapery or the flesh paint.
- 14 The sample was from the purple paint at the left edge. The major dyestuff was identified as kermes, from the scale insect *Kermes vermilio* Planchon. Minor amounts of methylated pseudopurpurin and purpurin (but no alizarin) were detected, indicating a very small quantity of a pseudopurpurin-rich madder, presumably from *Rubia tinctorum* L. A trace of ellagic acid was also detected, indicating that at least one of the lakes has been prepared by extracting the dye from the shearings of a silk textile.
- 15 See N. Penny in London 2003, p. 80, for discussion of this costume.
- 16 Some fading has certainly taken place, as can be seen from a more intensely red band of paint along the left edge where it has in the past been protected by a frame.

#### Cat. 7 *Noli me Tangere*

- 1 During the cleaning a small branch that had been added to the right side of the tree over the sky, in the position of Titian's larger suppressed branch, and alterations made by a restorer to the Magdalen's waistline and bulky draperies were removed. There are no large losses but the paint film is somewhat worn, especially in the sky. The suppressed branch had become obtrusively visible and was touched out again. The varnish applied in 1958 is now slightly discoloured.
- 2 N. Penny in London 2003, p. 86, and A. Bradley and D. Jaffé in London 2003, pp. 92–4, for the date of *Sacred and Profane Love*. See also M.G. Bernadini, 'L'"Amor Sacro e Profano" nella storia della critica' in Rome 1995, pp. 35–51.
- 3 The appearance of the buildings in the background of the Venus is not an obstacle to a date of around 1514 for all three paintings, and also the likelihood that they were devised initially for the *Noli me Tangere*, if it is accepted that the very damaged Dresden canvas is not the painting seen by Marcantonio Michiel and described as begun by Giorgione and on his death finished by Titian; see Joannides 2001, pp. 179–84.
- 4 Although there is a great deal of old putty and restoration around the edges, remnants of tack holes can be seen around all four sides.
- 5 Confirmed by SEM–EDX and ATR–FTIR microspectroscopic imaging. Although translucent colourless dolomite (calcium magnesium carbonate) is spread throughout the layer, only the one or two larger particles are easily seen, such as that at the far right of the cross-section that has the characteristic right-angled shape. Gypsum (calcium sulphate dihydrate) was confirmed in the gesso ground by FTIR microscopy in transmission mode.
- 6 In earlier reflectograms – published as details in J. Dunkerton, 'Titian's Painting Technique' in London 2003, pp. 51–2, and Dunkerton and Spring 2003, p. 15 – the underdrawing for Christ's features could not be seen.
- 7 For evidence of the use of a palette knife to scrape off excess *imprimitura* on the canvas of *Jacopo Pesaro being presented by Pope Alexander VI to Saint Peter* see Dubois and Wallert 2003,

- p. 24. Marks in the gesso on the *Portrait of Girolamo Fracastoro* (see essay, FIG. 13) indicate that it too was applied with a knife.
- 8 The X-ray and infrared images of the shepherd's breeches and leggings in *The Holy Family with a Shepherd* (CAT. 4) show similar ragged dark shapes where the paint may have pulled up while worked vigorously with the brush and perhaps also a knife.
  - 9 Gould 1958, p. 44. This interpretation was first questioned, before the underdrawing was revealed by infrared reflectography, by J. Dunkerton and N. Penny in Rome 1995, pp. 364–7, and then, with infrared reflectography, by J. Dunkerton, 'Titian's Painting Technique' in London 2003, pp. 51–2, and Dunkerton and Spring 2003, p. 15. There remains, however, a lingering attachment to the legs; see Washington and Vienna 2006, p. 130, and Rome 2013, p. 59.
  - 10 No pure white passages of drapery were sampled, so the binding medium of the white paint has not been identified. However, in both *The Holy Family with a Shepherd* (CAT. 4), and *The Music Lesson* (CAT. 12), GC–MS analysis of samples from white drapery paint identified heat-bodied walnut oil. It may be that, in this picture also, a heat-bodied walnut oil medium was used for the white despite the use of heat-bodied linseed oil in other colours (see also essay, p. 24).
  - 11 HPLC analysis identified the major dyestuff as kermes from the scale insect *Kermes vermilio* Planchon. Minor amounts of methylated pseudopurpurin and purpurin were also present, indicating a very small quantity of a pseudopurpurin-rich madder, presumably from *Rubia tinctorum* L. No alizarin was detected, but in any case it is often only a minor component in madder lakes at this date. An alumina-based substrate was confirmed by EDX analysis for the kermes lake.
  - 12 GC–MS analysis of the grey paint of the cloudy sky, the green and opaque brown foliage of the tree, as well as the more translucent yellow-brown foliage, identified heat-bodied linseed oil as the binding medium.
  - 13 Gould 1958, pp. 47–8. 'Copper resinate' is a term that has generally been used in the past for copper-containing glazes, whether browned or still green, and whether or not the full composition has been confirmed by analysis. Indeed, in 1958 this type of analysis was not possible. It was a prevailing belief at the time, which still persists to some extent, that a copper pigment such as verdigris was boiled together with an oil resin varnish to make 'copper resinate' which was either applied while still runny or ground to be used as a pigment after it had cooled. See Eikema Hommes 2004 for the historical origins of this belief and a review of documentary sources on green glazes. It is now known that these translucent paints are generally composed of verdigris, which has often reacted with the oil medium. A little oil-resin varnish is sometimes added, which can result in small amounts of copper-resin acid compounds ('copper resinate') being formed over time.
  - 14 FTIR microscopy in transmission mode identified dolomitic yellow earth and silicates associated with the earth, as well as a little verdigris.
  - 15 FTIR microscopy in transmission mode on scrapings of the paint of the opaque brown leaves, and ATR–FTIR imaging and SEM–EDX analysis of the cross-section in FIG. 126, from an adjacent area, confirmed a dolomitic yellow earth, red earth, indigo and verdigris. The verdigris particles appear rather brownish and may have discoloured. In addition EDX mapping indicated copper was spread throughout the layer, perhaps in the form of the copper soaps seen by transmission FTIR, a result of reaction of the pigment with the oil.
  - 16 Confirmed by FTIR microscopy in transmission mode and SEM–EDX on scrapings of green paint. FTIR showed unreacted particles of verdigris, as well as some sign of reaction with the oil in the form of some copper soaps. GC–MS analysis of the green leaves showed a higher than normal level of oleic acid, as is often seen in paint films containing verdigris that has reacted to form copper soaps. There was no indication of copper resinate.
  - 17 Although a translucent brown layer is visible at the surface of the cross-section in FIG. 126, FTIR and EDX analysis confirmed that directly on the paint is a calcium oxalate-type crust, on top of which is a layer which fluoresces under ultraviolet light, does not contain copper, and is probably the remains of a very degraded varnish not removed during the last cleaning, confirmed by the traces of mastic and pine resin that were just detectable by GC–MS analysis. Photomicrographs confirm that in some places on the tree tiny fragments of a discoloured yellow-brown varnish remain lodged in the interstices of the canvas weave.
- ### Cat. 8 *Bacchus and Ariadne*
- 1 An account of the treatment and condition is given in Lucas and Plesters 1978, pp. 25–37.
  - 2 For a brief account of the Camerino see London 2003, pp. 101–2. See also Gould 1969, pp. 9–12, and Gould 1975, pp. 268–74.
  - 3 Crowe and Cavalcaselle 1877 (1881) vol. I, p. 258.
  - 4 Gould 1975, p. 271. See also Lucas and Plesters 1978, p. 25.
  - 5 The gesso layer, confirmed as calcium sulphate, was included in five samples (from a total of 25 samples). In these five, cross-sections seemed to show an extremely thin grey layer above the gesso, which may be a priming but could also simply be part of the paint layer structure. In any case it is quite unlike the thicker pale grey priming layers seen on other early paintings (see essay, pp. 11–16).
  - 6 In Bull and Plesters 1990 *The Feast of the Gods* was described as having a lead white priming, but during this study it was possible to re-examine a sample stored in the Scientific Department and under the better microscope now available it could be seen that in addition to lead white the priming layer contains lamp black and a little yellow earth. SEM–EDX analysis confirmed the latter and also showed that the small translucent particles that were present were dolomite (calcium magnesium carbonate) associated with the yellow earth.
  - 7 Illustrated in Lucas and Plesters 1978, p. 34. Drawings made by workshop members are often found on the backs of panels, including some by Titian, the best examples being those on the Pala Gozzi in Ancona; M. Cordaro, C. Giantomassi and D. Zari, 'Il restauro del dipinto' in Ancona 1988, pp. 72–3. There are also sketches on the back of the canvas of the *Annunciation* (Scuola Grande di San Rocco, Venice); see Venice and Washington 1990, p. 214.
  - 8 This has resulted in dark areas in the X-radiograph that have the appearance of paint losses but are actually the result of flaking of the lead white on the reverse; see Lucas and Plesters 1978, pp. 35–6. Elsewhere the presence of this layer reduces the contrast between areas where paint containing lead white had been thickly applied and those that are more thinly painted or contain X-ray transparent pigments. In addition, the overlaps between X-ray plates were insufficient for a completely accurate mosaic to be assembled. Unfortunately, it is not possible to X-ray the painting again as the composite panel to which it is attached includes a honeycomb core which would disrupt the image even more than the lead white layer.
  - 9 The pigment mixtures for this figure contain so little lead white that he barely registers in the X-radiograph. The only strong highlights are those on the snakes that entwine him.
  - 10 In October 1522 Titian told Giacomo Tebaldi, Alfonso's agent (who was putting pressure on him to finish the work), that he just had to change two women and the painting would be ready; see Gould 1975, p. 270. Perhaps he was still adjusting Ariadne. The other woman may be the girl with the tambourine, whose drapery was reduced.
  - 11 See Lucas and Plesters 1978.
  - 12 Bellini also followed this practice in the dress of the nymph in the centre of *The Feast of the Gods*. Bull and Plesters 1990, p. 63.
  - 13 Lucas and Plesters evidently already considered that the azurite and white layer was indicative of a pentimento, since they interpreted it as the greenish-blue paint of the sea. The sample is in fact from a point above the horizon, so if this layer is background paint then it is more likely to be the underpaint of the sky (as seen in other samples). It is not known whether azurite is present beneath ultramarine in Ariadne's blue drapery since no sample was taken, but Titian generally seems to have used other pigments in the underpaint for blue draperies.
  - 14 The d'Este family seems to have had an obsession with obtaining the highest quality ultramarine for use in their commissions. This

goes back at least to the Muses for Lionello and Borso d'Este's Belfiore Studiolo; see Dunkerton, Roy and Smith 1987, p. 34, note 31.

- 15 The sample was from the top of her thigh, very close to where the two sides of her skirt part on either side of her leg, and the infrared image does show shifts in contours in this area that could explain these overlapping paint layers. The pigments were analysed by SEM-EDX on the cross-section.
- 16 This cross-section is reproduced in Plate 6c in Lucas and Plesters 1978. The second of the pink layers was described as white in this article, but with the better microscope now available it is clear that it is pink. SEM-EDX detected Al in the red lake pigment.
- 17 Confirmed by SEM-EDX analysis. The high quality of the pigment is evident in the small proportion of associated colourless minerals relative to blue lazurite. A little potassium feldspar was detected, as well as a silicate containing Si, Al, Mg and K, which may be phlogopite, and one particle of pyrite (FeS<sub>2</sub>). The lazurite particles are around 10 µm in size on average.
- 18 These include works produced in Rome by Sebastiano del Piombo; see Dunkerton and Howard 2009, pp. 36–7.
- 19 Arsenic and sulphur were confirmed to be present in the bright orange-yellow particles by SEM-EDX. Raman microscopy identified mainly pararealgar, which is yellow, with some realgar. We are grateful to Janet Ambers at the British Museum for this analysis. For further discussion see essay, p. 30.
- 20 SEM-EDX confirmed a dolomitic yellow earth, a very small amount of arsenic sulphide and lead white in the underpaint in a light tone of the drapery. In a darker tone there seems to be red earth in addition in the underpaint, as well as one or two black particles that were confirmed by SEM-EDX to be coal black. The upper orange paint layer in the darker tone was composed of arsenic sulphide pigment mixed again with dolomitic yellow earth and red earth, as well as one particle of ilmenite (FeTiO<sub>3</sub>) which may be associated with the red earth, as it was found to be in *The Flight into Egypt* (CAT. 1, note 13).
- 21 This sample is also illustrated in Lucas and Plesters 1978. The uppermost layer was said to contain malachite, and the lower dark green layer green earth. Analyses with SEM-EDX and ATR-FTIR imaging on this same cross-section have now, however, made it possible to confirm the new pigment identifications. The lead-tin yellow is inhomogeneous, with tin-rich zones that are probably unreacted white tin oxide, as found in other paintings in this study (see also note 22).
- 22 Identified by X-ray diffraction as lead-tin yellow of the 'type I' form. In a cross-section it can be seen that there is extensive lead soap formation, and SEM-EDX analysis indicated that the pigment was inhomogeneous, with tin-rich zones of white unreacted tin oxide, perhaps accounting for the rather pale tone of the yellow (see also note 21).

#### Cat. 9 *Portrait of Girolamo Fracastoro*

- 1 For the identification of the sitter and the date of the portrait see Dunkerton, Fletcher and Joannides 2013.
- 2 Identified by EDX analysis. Some dolomite (calcium magnesium carbonate), calcium carbonate and a significant amount of celestite (strontium sulphate) are also present.
- 3 EDX analysis detected a significant amount of sulphur (in addition to carbon) in this pigment, which is characteristic of coal black, as is its appearance under the microscope. Although coal black was a relatively common pigment in the sixteenth century (see Spring, Grout and White 2003, esp. pp. 97–100), this does make it more likely that the doorway is an original feature.
- 4 Identified by GC-MS analysis. The azelate/suberate ratio obtained from the paint of the cloak was of an intermediate level: not as low as that expected for a heat-bodied oil but not as high as that expected for a non heat-bodied oil. The ratio obtained from the sample within the archway was slightly closer to that expected for a heat-bodied oil, but was again a little high.
- 5 Identified by GC-MS analysis, although some caution is required in the interpretation of the results due to a little beeswax contamination from the lining process. The sample from the ledge appears to be a heat-bodied oil, but the azelate/suberate

ratio obtained from the sample from the architectural feature lies between that expected for a heat-bodied and a non heat-bodied oil.

#### Cat. 10 *A Boy with a Bird*

- 1 For a detailed account of the condition, technique and discussion of the connections between this painting and the Venus and Adonis paintings see Joannides and Dunkerton 2007, pp. 36–57. Joannides favours an earlier date of around 1516 to that suggested here.
- 2 Gould 1975, pp. 298–9.
- 3 Usually identified as the canvas now in the Museo Nacional del Prado, Madrid.
- 4 The complex argument is presented, with extensive illustration by Joannides, in Joannides and Dunkerton 2007, pp. 36–41; see also Joannides 2008, p. 46, and Joannides 2006, pp. 141–5.
- 5 Illustrated in Joannides and Dunkerton 2007, p. 45.
- 6 Suida 1932, pp. 164–6. Reproduced in Joannides and Dunkerton 2007, p. 38. Other copies and versions also existed; see Joannides and Dunkerton 2007, p. 54, note 2.
- 7 EDX analysis detected manganese and oxygen in the black particles, identifying them as pyrolusite, manganese dioxide. Iron was present in the red and yellow particles in the ground, confirming earth pigments. Associated potassium aluminium silicates and silica were also found, as well as particles containing calcium. X-ray powder diffraction confirmed the presence of iron oxide, calcium carbonate and silica as the major components.
- 8 In several of the samples this pigment is in the form of large agglomerates, in which EDX analysis detected, in addition to manganese dioxide, some barium sulphate. The latter is a common accessory mineral associated with pyrolusite. For the use of natural mineral form of manganese dioxide in sixteenth- and seventeenth-century painting see Spring, Grout and White 2003, pp. 100–1.
- 9 Dunkerton and Spring 1998, p. 122.
- 10 In Humfrey 2004, p. 92, it is dated c.1520, but in London 2003, in the caption to fig. 46, p. 94, it is dated c.1530.
- 11 If so, the canvas must have been recently primed and painted in order for weave distortion to have occurred when the smaller piece was stretched.
- 12 The possibility that Titian and his workshop were producing landscape paintings closely related to the woodcut is suggested by the inclusion of such a painting as part of the stock of the eighteenth-century Paris dealer Gersaint, in a strip added by an anonymous painter to the top of Watteau's famous shop sign only a few years after it was first painted; see Joannides and Dunkerton 2007, p. 56, note 47. Of course, this could be an invention based on the print.
- 13 Identified by FTIR microscopy.
- 14 Identification of the pigments in these mixtures was made on the basis of SEM-EDX analysis. The suggestion that yellow lake might be present is based on the detection of calcium carbonate in these layers, which could be a substrate for this pigment.
- 15 Analysis was carried out by GC-MS and the results were reported in Joannides and Dunkerton 2007, p. 52. The presence of a small amount of beeswax contamination in some samples led to a rather cautious interpretation of the detection of walnut oil at this time; see especially note 62. However, after recent reassessment of these results we can state more confidently that walnut oil was used as the binding medium in the pink paint from the boy's finger and the white paint of his sleeve.
- 16 There was some small variation in each sample of the ratio of the di-acids azelate and suberate, used as a guide to the degree of heat-bodily. In most cases this fell within the range expected for a heat-bodied oil. However, it was slightly higher for the sample from the sky, although not high enough to indicate a non-bodied oil.
- 17 GC-MS analysis of this sample gave a slightly lowered azelate level, possibly due to a small amount of beeswax contamination; however, the identification of linseed oil is clear. The azelate/suberate ratio was again a little higher than that expected for a heat-bodied oil, but not high enough to suggest a non-bodied oil.

Cat. 11 *The Virgin and Child with the Infant Saint John and a Female Saint or Donor ('The Aldobrandini Madonna')*

- 1 The painting is generally in good condition, with damage limited mainly to the edges and to the upper part where it was once turned over onto a smaller stretcher. During restoration the intense blue of the distant mountains was apparently toned down by retouching. Uneven residues of darkened old varnish disrupt the modelling in some places: for example, the Child's proper left hand. Retouchings on the female saint's skirt are mismatched or discoloured and the varnish applied in 1955 has become a little blanched. This is especially evident over the deepest folds of the Virgin's mantle. It is possible that there has also been some degradation of the ultramarine blue glazes.
- 2 For the provenance see Penny 1999, pp. 111–12.
- 3 See Gould 1975, p. 278, although he was inclined not to identify this with the National Gallery canvas as he believed that the saint is Saint Catherine. In the National Gallery Catalogue of 1860/1 (Wornum 1860, vol. I, p. 258) the painting is recorded as inscribed: 'TICIANUS' and the date 1533. Although there is no record of any cleaning until that of 1955, there was no inscription by then. It can hardly have been original and may well have been fictitious.
- 4 Penny 1999, pp. 111–12. It seems to have been a common practice to extend paintings in the Spanish royal collections by stitching on pieces of canvas; see Z. Véliz, 'The Restoration of Paintings in the Spanish Royal Collections, 1734–1820' in Sitwell and Staniforth 1998, pp. 47–8.
- 5 R. Bellucci and C. Frosinini, 'Considerazioni sul disegno e "underdrawing" nella pittura veneta e in Tiziano' in Florence 2011, pp. 57–60. In the case of the Fort Worth version, the X-radiograph shows that the central group was initially closer to the London painting, with the same pose for the Child and a figure on the left in the same position as the young Baptist. This is very blurred in the X-radiograph and it has been suggested that it might be an angel. The head of the Baptist on the right appears to cross the dense green paint of the landscape, and so he too may be a later introduction. See Christiansen 1987, pp. 190–6. A third, less close, variant is a panel in the Royal Collection. It is smaller but the omission of the Baptist and female saint meant that the traced cartoon from the National Gallery painting could still be used for the Virgin. The figure of the Virgin and the rather tightly painted landscape detail are almost certainly not by Titian, but he may have contributed the wriggling Christ Child and the figures of Tobias and the Angel in the background. See London 2007, pp. 194–7, and Izat 2006, pp. 43–52.
- 6 See M. Falomir, 'Titian's Replicas and Variants' in London 2003, pp. 60–8; R. Wald, 'Tizians Wiener Danae. Bemerkungen zur Ausführung und Replikation in Tizians Werkstatt' in Vienna and Venice 2008, pp. 123–31.
- 7 Spot spectra of larger black particles in the *imprimitura* collected during SEM–EDX analysis gave large peaks for manganese. EDX mapping of the large particle in this layer in FIG. 172 indicated that iron was located in the brown areas and manganese in the black areas.
- 8 The painting was examined with infrared in 2005 using a Hamamatsu vidicon but only small areas of particular interest were recorded. As a result less can be said about more general features as seen by infrared imaging of the other paintings in this study.
- 9 See, for example, Penny 1999, p. 109.
- 10 Careful notes and a coloured drawing of the cross-section by Joyce Plesters in 1955 record the layer structure and paint composition. She also noted that although the priming and gesso ground were not present in the cross-section, other small paint fragments indicated that the rose pink was directly on the *imprimitura*. Although the cross-section survives and this layer structure can still be recognised, it is not in good enough condition to illustrate here. A further sample taken from this drapery in 1993 included only the uppermost yellow paint. X-ray diffraction confirmed that the lead-tin yellow was of the 'type I' form (matching the JCPDS pattern no. 384).
- 11 The yellow is very pale and as in other paintings in this study this

seems to be because some white tin oxide is present in the lead-tin yellow, indicating incomplete roasting during manufacture of the pigment. Extensive lead soap formation is also evident in the cross-section.

- 12 SEM–EDX analysis showed that the pigment includes only a small proportion of associated colourless minerals relative to blue lazurite, indicating a high-quality pigment. When the sample was taken in 1993 it was noted that the paint might be degraded. The blue pigment itself, averaging 5–10 µm in particle size, is still an intense colour, but in the backscattered electron SEM image the paint as a whole appeared notably porous, which might explain its slightly blanched appearance.
- 13 In some of the large verdigris particles a small amount of chlorine was detected in addition to copper, probably related to the method of manufacture. The lead-tin yellow includes pale tin-rich zones indicating incomplete roasting of the raw materials, as also seen in some of the other paintings.
- 14 SEM–EDX mapping detected copper in this layer. ATR–FTIR microspectroscopic imaging confirmed that verdigris was present. A band in the FTIR spectrum at around 1607 cm<sup>-1</sup> might also be related to the verdigris pigment, or might indicate the presence of some 'copper resinate' as a reaction product, either with varnish on the surface or with resin in the paint medium, although the many overlapping bands in the spectrum from different components make it impossible to be certain about the assignment.

Cat. 12 *The Music Lesson*

- 1 For the provenance see Penny 2008, pp. 296–303 (catalogued as After Titian, with a date of c.1580); also summarised in Dunkerton, forthcoming.
- 2 Dunkerton, forthcoming.
- 3 See Penny 2008, pp. 296–303.
- 4 The gesso ground was identified as calcium sulphate on the basis of EDX analysis (Ca, S, O detected). EDX analysis of the pigments in the priming showed the presence of lead white, a very small amount of vermilion and black, larger amounts of earth pigments (mainly yellow or yellow-brown in appearance, but with one large agglomerate of red earth in one sample). Some particles proved to be iron-rich, others contained some manganese in association with iron. Associated siliceous particles containing Si, Al, Fe, Mn, Ca, Mg and K were also found. Some particles containing Ca, C and O were identified, and the presence of calcium carbonate was confirmed by FTIR in transmission mode, as was lead white in the form of both hydrocerrusite and cerrusite. The binding medium was identified by GC–MS.
- 5 Transmitted infrared imaging was carried out with the light source and OSIRIS camera on opposite sides of the canvas, which was temporarily stretched on a loom. Two images were made: one with the camera facing the back of the canvas and the other with the camera facing the painted surface. In the absence of sufficient comparable images it is not easy to interpret the results of this form of infrared imaging, but in this instance it was useful as features became apparent or were more easily recognised than by conventional reflectography.
- 6 Dunkerton, forthcoming.
- 7 Dunkerton, forthcoming.
- 8 FTIR analysis in transmission mode identified lead white of the hydrocerrusite and cerrusite form, and confirmed the presence of calcium carbonate and silicates; the latter must be associated with the earth pigments, the former is possibly a separate addition.
- 9 C. Lalli, G. Lanterna, I. Tosini, D. Andrash and F. Innocenti, 'Le analisi del Laboratorio Scientifico dell'Opificio delle Pietre Dure su 'La Bella' di Tiziano' in Florence 2011, p. 90.
- 10 Pigment identification confirmed by EDX analysis. There is only a very small amount of red pigment present, but a similar use of a little red lake in green paint has been reported in other paintings by Titian. See Izat 2006, p. 49.
- 11 Confirmed by EDX analysis, which also showed that the lead-tin yellow was inhomogeneous and incompletely roasted so that there are tin-rich zones present (see essay, p. 30).
- 12 For discussion of the costume, which is clearly theatrical fancy dress, see Dunkerton, forthcoming.

- 13 HPLC analysis identified kermes from the scale insect *Kermes vermilio* Planchon. Smaller quantities of methylated pseudopurpurin and purpurin were also detected, with a trace of alizarin, indicating the presence of a pseudopurpurin-rich madder, presumably from *Rubia tinctorum* L. In addition, traces of an unidentified component, often known as 'Nowik Type C', reported to be found in samples of soluble redwood from species of *Caesalpinia*, were detected, indicating that some brazilwood or sappanwood may also be present. See Nowik 2001.
- 14 Confirmed by EDX analysis. In some black particles Mn was the predominant element, confirming manganese black which must be natural pyrolusite. The calcium carbonate could be an extender, or might instead be present as a component of the earth pigment.
- 15 The ATR-FTIR spectra include bands at *c.*1548 and *c.*1411  $\text{cm}^{-1}$ , characteristic of the acetate ion, presumably copper acetate since copper was confirmed by EDX analysis. An additional band at *c.*1612  $\text{cm}^{-1}$  was also present which is difficult to assign but seems to be characteristic of the particles with this appearance.
- 16 The calcium carbonate found in this layer could be associated with the earth pigment, which EDX analysis indicated consisted of iron-rich yellow particles and associated silicates. The EDX also showed that there is a small amount of bone or ivory black present, but the larger black particles seemed to have the characteristics of coal black.
- 17 Analysis by GC-MS detected heat-bodied linseed oil as the binding medium of the upper brown layer. Although some peaks for diterpenoid resin acids were observed, these could be connected to traces of varnish; the absence of components such as retene, hydroretene and norabietatrienes suggests that no pitch was present in the sample.
- 18 This is consistent with the observation that a large blackish particle appeared translucent brown when compressed in the diamond cell for FTIR analysis. The spectra from both the large black particles and the smaller brown particles were characterised by a broad peak with a maximum at *c.*1616  $\text{cm}^{-1}$  which can be related to the aromatic ring stretching. FTIR spectra of this type are also seen more generally in brown or black pigments derived from fossilised or pyrolysed materials, such as lignitic earths or bistre produced from wood soot. However, although the presence of some other organic pigment in addition cannot be ruled out, it is most likely that they are smaller particles of coal black since larger particles of this pigment certainly are present.
- 19 Medium analysis was carried out by GC-MS.
- 20 Mills and White 1977, p. 58.

### Cat. 13 *The Triumph of Love*

- 1 See 'Recovering Titian: The Cleaning and Restoration of Three Overlooked Canvas Paintings', pp. 106–21.
- 2 For a full account of the provenance, function as a portrait cover and sources for the design see Whistler 2009, pp. 536–41.
- 3 See also Dunkerton 2009, p. 542.
- 4 See Penny 2004, pp. 99–101.
- 5 Whistler 2009, p. 536.
- 6 For the date and extended execution of *The Vendramin Family* see Penny 2008, pp. 206–35.
- 7 A sample from the sky at the left edge, which coincides with a line for the oculus that can be seen in the infrared image, shows that this particular line of drawing lies on top of the first indigo and lead white underpaint of the sky (FIG. 233, p. 118).
- 8 Identified by GC-MS analysis.
- 9 Indigo was identified by transmission FTIR microscopy on a small fragment of the underlayer from a sample of the distant landscape to the right of Cupid. An underlayer of the same composition is also visible in cross-sections from the sky and the landscape on the left of the painting.
- 10 Lead-tin yellow was identified by SEM-EDX analysis. It is in the form of large agglomerates, which has perhaps prevented the starting materials from fully reacting when they were roasted, since by EDX mapping it can be seen that these include pale zones rich in tin, which are probably unreacted tin oxide. This makes the pigment a rather pale yellow.
- 11 A similar effect, where the verdigris glaze is well preserved when

applied over an opaque green underpaint in the landscape, and discoloured when applied over a lighter layer, can be seen in two other paintings in the National Gallery: Jacopo Bassano's *The Good Samaritan* (NG 277) and Paolo Veronese's *Respect* (NG 1325). See Dunkerton and Spring, forthcoming; and Penny, Roy and Spring 1996.

- 12 The texture must be the result of the lead-tin yellow having formed large agglomerates, as seen in a sample and also discussed in note 10.

### *Recovering Titian: The Cleaning and Restoration of Three Overlooked Canvas Paintings*

- 1 Wethey 1969–75, vol. III, pp. 220–1. For its recent history of attribution see Whistler 2009, p. 536, note 2.
- 2 For the attribution of the *Portrait of Girolamo Fracastoro* see Dunkerton, Fletcher and Joannides 2013, p. 4; and for *The Music Lesson* see Penny 2008, pp. 296–301, and Dunkerton, forthcoming.
- 3 Suida 1933, p. 52 (for the portrait), and Suida 1935, p. 184 (for *The Music Lesson*).
- 4 Dunkerton, Fletcher and Joannides 2013.
- 5 For Girolamo Romano and Teodoro Lechi see Penny 2004, pp. 381–2.
- 6 Unfortunately contamination of a sample with wax from later conservation treatments meant that analysis was not successful.
- 7 The relining was carried out by David Thomas of the National Gallery Conservation Department.
- 8 In order to achieve maximum saturation of the damaged dark colours the surface was first varnished with 'Regalrez 1094'. The losses were retouched with 'Gamblin Conservation Colours' and glazed, if necessary, with pigments ground in 'Regalrez 1094'. The final sprayed varnish is 'MS2A'.
- 9 For the frame see Penny 2010, pp. 59–61.
- 10 For a fuller account of its provenance and reputation see Penny 2008, pp. 296–301, and Dunkerton, forthcoming.
- 11 Stretchers of this construction have been noted on several English paintings. The stretcher of Joshua Reynolds's *Portrait of the 4th Duke of Queensbury ('Old Q') as Earl of March* in the Wallace Collection, which is likely to have been lined in London in the late eighteenth or early nineteenth century, is very similar. Another example is the stretcher that was present on Wright of Derby's *Mr and Mrs Thomas Coltman* (NG 6496) when it was acquired by the National Gallery. This may date from 1826. See Wyld and Thomas 1986, p. 29. I am grateful to Alexandra Gent for discussion of this point.
- 12 This observation was made in the entry for the painting in the newly compiled 'Manuscript Catalogue'.
- 13 National Gallery Conservation Record, transcribed from the 'Manuscript Catalogue'.
- 14 Crowe and Cavalcaselle (1877) 1881 vol. II, pp. 459–60.
- 15 Penny 1997, p. 300. In 2002 it was exhibited in Mantua as 'Padovanino?'. See note 16 below.
- 16 For the catalogue entry see Mantua 2002, vol. 1, p. 194.
- 17 National Gallery Conservation Record for NG 3.
- 18 During cleaning it was discovered that the same dark grey putty covered the extensions and was smeared over flake losses in the main part of the painting. The solubility of the putty and the retouchings over it indicated that that it was unlikely to be from an earlier restoration. The format of the best of the painted copies of the work, possibly even by Padovanino and illustrated in Penny 2008, p. 300, is close to that of the National Gallery canvas without the extensions. Two engravings made when the painting seems to have been in Holland in the later seventeenth and early eighteenth centuries are slightly extended at the right side (or left side in the case of the Gronsveld print which is reversed) in order to include more of the scroll of the viol, but such adaptations are common in reproductive prints and they are not always a good guide to the original dimensions of altered paintings.
- 19 In Penny 2008 it was still catalogued as 'Imitator of Titian' but with the date brought forward to *c.*1580.

- 20 When acquired for the collection of Charles I, the painting must have been among the consignment of works shipped from Italy to London on The Margaret. Some of these were apparently irretrievably damaged by contact with a leaking cargo of mercury. Several paintings had to be cleaned by Jerome Lanier, brother of Nicholas, as mercury vapour seems to have blackened the surfaces. It seems that some could be surface cleaned with saliva or warm milk, but with others the varnishes had to be removed and replaced. Lanier stated that he used aqua vita (also known as 'spirits of wine'), which is distilled alcohol with a high water content, in other words a fairly powerful solvent for varnishes; see I. McClure, 'The History of Painting Conservation and the Royal Collection' in Sitwell and Staniforth 1998, pp. 85–96.
- 21 GC-MS analysis detected norambreinolide, a characteristic component of fir balsam, along with additional diterpenoid resin acids. Fir balsam is mentioned as a varnish ingredient in several nineteenth-century recipes. It has been found on other National Gallery paintings, usually as part of a varnish layer applied prior to acquisition by the National Gallery or during a treatment carried out in the nineteenth century. See White and Kirby 2001.
- 22 The consolidation and relining were carried out by Paul Ackroyd and Lynne Harrison.
- 23 Illustrated in Penny 2008, p. 296.
- 24 This number does not relate to its number in the Gonzaga and Royal Collection inventories of 1626 and 1650.
- 25 See note 18 of this essay.
- 26 The filling is a liquid 'gesso' made from chalk and polyvinyl alcohol and the 'imprimatura' is based on pigments ground in 'Paraloid B-72' with some 'Art Care B72 Retouching Gel' added to texture the filling and retouching so that the restoration scatters light in a similar way to the cracked original paint surface. The retouching was carried out with 'Gamblin Conservation Colours' with some glazes with pigments ground in 'Regalrez 1094'. The paint film proved easy to saturate following relining and so 'MS2A' was used as the preliminary and final varnish. This varnish also has the advantage of not being too brilliant and glossy, which can result in surface sparkle on a painting such as this with slightly elevated edges to the craquelure.
- 27 A detail is illustrated in Penny 2008, p. 302.
- 28 Penny 2008, p. 299.
- 29 Anderson 1979, p. 647, subsequently associated with the painting under discussion; see Humfrey 2007, p. 217.
- 30 Whistler 2009, pp. 536–42.
- 31 Whistler 2009, p. 536.
- 32 Kirby and Saunders 2004, p. 82.
- 33 Garnett 2000, p. 184.
- 34 For the manufacture and appearance of the eighteenth-century pigment see Kirby and Saunders 2004, pp. 79–81. It is easy to see the attraction for Sasso of adding some of this relatively cheap pigment to expensive natural ultramarine in his retouching paint (the artificial form had yet to be invented).
- 35 Whistler 2009, p. 536.
- 36 The treatment of the panel was carried out by David Thomas of the National Gallery Conservation Department.
- 37 The losses were retouched with 'Gamblin Conservation Colours' and the painting varnished with 'Regalrez 1094'.
- 38 Dunkerton, Fletcher and Joannides 2013, p. 7, note 19.
- 39 For discussion of *timpani* with further references, see Penny 2004, pp. 99–101.

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