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Paintings in the laboratory: scientific examination for art history and conservation

dr. Groen, C.M.

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Vermeer Studies



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Frontispiece: Johannes Vermeer, *Woman Holding a
Balance* (detail), c. 1664, oil on canvas. National
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Vermeer Studies

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KARIN M. GROEN, INEZ D. VAN DER WERF,
KLAAS JAN VAN DEN BERG, and JAAP J. BOON
Netherlands Institute for Cultural Heritage and FOM Institute for Atomic and
Molecular Physics (AMOLF), Amsterdam

Scientific Examination of Vermeer's Girl with a Pearl Earring

The background of the *Girl with a Pearl Earring* seems to be exceptional in Johannes Vermeer's oeuvre (fig. 1); the only picture with a comparable dark background is *Portrait of a Young Woman* (in New York), dated c. 1666–1667. Arthur K. Wheelock Jr. points out that Vermeer's departure from his normal scheme of silhouetting figures against a white wall was according to the Dutch tradition and was meant to enhance the three-dimensional effect. White backgrounds tend to come forward while dark backgrounds tend to recede, bringing the figure into prominence.¹

Presently the background of the *Girl with a Pearl Earring* appears uneven and spotted. During the 1994–1995 restoration it became clear that this appearance has nothing to do with ornamentation as, for example, is the case with the background of *The Girl with the Red Hat*. The poor state of the painting may be related to earlier restoration procedures. It has been documented that the painting had been subjected to several lining and regeneration treatments. Investigation of the background was therefore undertaken as part of a larger study of the techniques and materials used by Vermeer in this painting.

In 1980 the picture was investigated non-destructively by J.R.J. van Asperen de Boer and Arthur K. Wheelock Jr. with infrared reflectography and a stereomicroscope. Dark underpaint was found under the shadows of the blue turban, the yellow drapery, and the flesh. A small change in composition was

found at the back of the neck. As early as 1968 two paint samples had been removed from the background along the left-hand and right-hand edges and analyzed by Hermann Kühn of the Doerner Institute in Munich.² Kühn had found a dark underlayer on top of a light-colored ground. The results of the investigations into the paint layers were scarce and necessitated further research.

This paper discusses the results of microscopic examination and chemical analysis of the background.³ In order to obtain more complete insight into the techniques and materials used by Vermeer, other parts of the painting are examined as well. Restoration materials introduced into the painting and the effects of former restoration procedures are also considered. Results of chemical analysis are presented to illustrate that these treatments have changed the chemical composition of the painting. The paint samples mentioned in this article can be found in appendix 1. See appendix 2 for a description of the analytical methods.

History and Condition of the Painting

The restoration history of the *Girl with a Pearl Earring* was, as far as noted down, discussed by Jørgen Wadum and others in 1995.⁴ The gist of their study is as follows. In 1903 the painting came into the possession of the Royal Cabinet of Paintings Mauritshuis as part of a bequest by A. A. Des Tombe of a total

1. Johannes Vermeer, *Girl with a Pearl Earring*, c. 1665–1666, oil on canvas, photographed June 1994, after cleaning, before restoration
Royal Cabinet of Paintings
Mauritshuis, The Hague

of twelve pictures. About twenty years earlier, in 1881, it had been recognized as a work by Johannes Vermeer. According to a newspaper article in the *Nieuwe Courant* in 1903, the painting was already in a "deplorable state of neglect" when it was in the possession of Des Tombe.⁵ The same article reports that it was lined by a certain Van der Haeghen in Antwerp. This restorer probably applied an aqueous adhesive, since the original canvas showed signs of bad shrinkage owing to contact with water. This shrinkage has resulted in "cupping" of the paint film. For the lining treatment, Wadum has suggested that starch was used.

A photograph taken in 1904 (fig. 2) shows that bits of paint had become dislodged before that date; the photograph shows retouching as well. From correspondence about the painting we know that it had been strongly overcleaned and that retouches were visible to the naked eye.⁶ In 1915 and 1922 the picture was restored again by Derix de Wild. His treatment mainly concerned the regeneration of the varnish layers.⁷ A second lining was carried out by J. C. Traas in 1960. This time a wax-resin mixture was used, after the removal of the previous lining.

During the 1994 examination it was confirmed that the picture had undergone rough handling in the past because numerous bits of paint were situated upside down on top of the paint surface. For example, a tiny, second highlight in the earring turned out to be such a displaced fragment.⁸ The exact original location of the disfiguring pieces of paint that were present on top of the picture surface was unknown. Nevertheless, they were removed and used for the study of Vermeer's painting technique and the possible causes of changes in the painting materials. Some of the pieces were found near their probable source; others were found far removed from it. The fragment containing a mixture that may only represent flesh color, for instance, was found to the right of the pendant of cloth cascading down from the knot at the top of the turban (sample 1687/4). In some pieces, two sets of original paint layers were sitting, face to face, on top of each other. One advantage of the unfortunate state of the picture was that the intentional removal of paint samples for examination could be limited. In all, thirty-eight chips of paint, including later added fillings



and samples from other restoration materials, were examined (appendix 1).

2. Johannes Vermeer, *Girl with a Pearl Earring* (detail), photograph taken in 1904, showing dislodged paint and retouchings

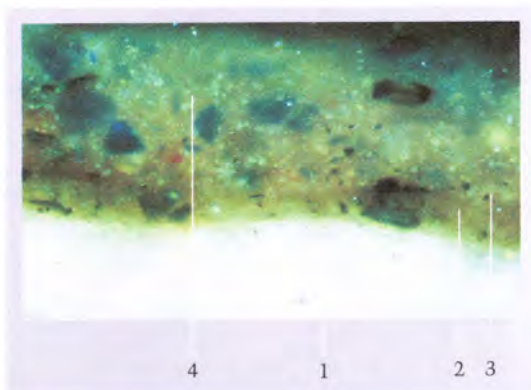
Ground and Underpaint

Ground

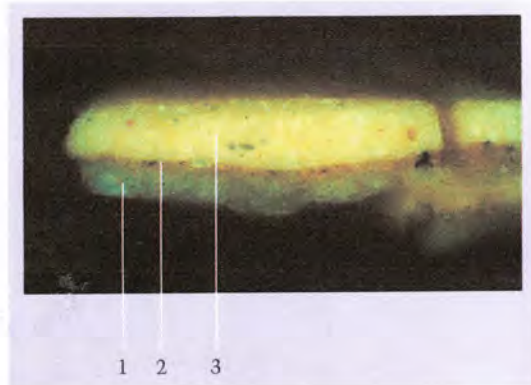
On examination with the naked eye, a rather dense, yellowish-white ground was observed. This layer, with a thickness of up to 200 micrometers (μm) (sample 1687/21), almost hides the structure of the canvas fabric. Judging from the x-radiograph, the paste used for the ground was applied with a knife rather than with a brush.⁹

Microscopic examination and Scanning

3. Paint cross section of sample 1687/22, shadow in blue drapery, right-hand side, 6 cm from the bottom edge of the picture, 4.1 cm from the right-hand side. Result: (1) >22 μm ground (photograph overexposed); (2) c. 7 μm bone black in grayish-brown medium; (3) 0–8 μm bone black, very little brown ocher in brown medium; (4) c. 40 μm natural ultramarine, carbon (bone?) black, very little of an organic red pigment, a little yellow, and brown ocher. Oil-immersion objective. Magnification 670x



4. Paint cross section of sample 1687/25 from the yellow jacket. (1) ground, contains lead white, chalk, very little brown and red ocher, very little very fine black; (2) c. 5 μm a dark layer of yellow, brown, and very little red ocher, a little finely ground charcoal black in brown medium; (3) c. 28 μm lead white, finely ground yellow ocher, very little brown ocher, and finely ground ultramarine. Magnification 305x



Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) showed that the ground is composed of chalk, lead white, some ocher, and a little very fine carbon black, possibly lampblack. The lead white shows large and small particles, typical of the so-called Dutch process,¹⁰ except that the pigment used by Vermeer seems more homogeneous and more finely ground. The binding medium was identified by Pyrolysis-TMAH-Gas Chromatography Mass Spectrometry (PY-TMAH-GCMS) as linseed oil (palmitic acid/stearic acid [P/S] ratio = 2.1).¹¹

Dark Underpaint

As noted above, Van Asperen and Wheelock found dark underpaint under the shadows of the blue turban, the yellow drapery, and the flesh. The black shines through the blue, yellow, and flesh paint, giving the yellow its greenish hue, for instance. A small change in composition was found at the back of the neck.

The presence of a dark underlayer was confirmed in our examinations of paint cross sec-

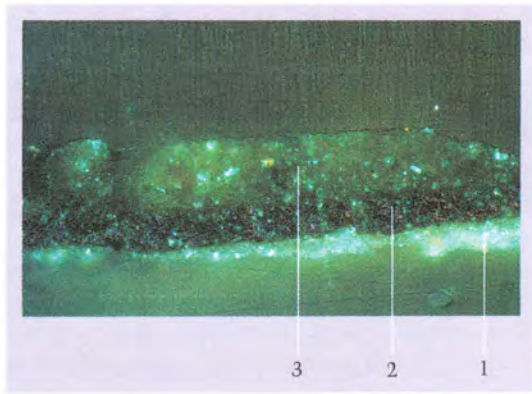
tions. Such a layer was found in both shadows and highlights in the painting. Under dark areas, however, the underpaint is thicker and brownish-black, consisting of bone black and some brown ocher (1687/19, 21–24, 26; fig. 3). In the lighter areas, a thinner layer containing yellow and brown and very little red ocher with a small addition of finely ground charcoal black is observed (1687/25, 28; fig. 4). Different carbon blacks in one painting give their own distinct effect, and several combinations can be found in old master paintings.¹² Fluorescence images and staining of paint cross sections containing the bone black layer indicate that the medium of this layer was oil rather than glue. In the sample from the shadow at the jacket (1687/22), two underlying dark layers were found; one of these two may be the paint used for sketching in the figure.

The purpose of the dark underpaint must have been to brush in a monochrome image on the smooth, light-colored ground.

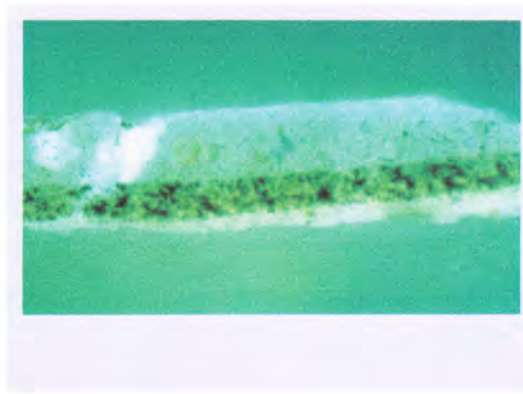
Paint Layers of the Figure

In most samples, only one paint layer was found on top of the brownish-black underpaint; occasionally there are two, wet-in-wet. Using this simple painting technique, Vermeer seems to have adjusted both the color and the thickness of the final paint layer and the brownish-black underlayer in order to obtain the desired effect. In the light areas, on top of the thin, dark underpaint there is a rather opaque top paint layer. In contrast, in dark areas the dark underpaint is thicker and the top layer more transparent.

Two representative examples of the constitution and composition of the draperies illustrate this. Sample 1687/22 (fig. 3) derives from the blue shadow in the drapery. The greenish-blue shadow was achieved with one layer of paint, c. 40 μm thick, containing a mixture of natural ultramarine, very little of an organic red pigment, chalk, some lead white, very little brown, and yellow ocher and black. The underpaint layer was discussed above. A sample from the yellow in the jacket (sample 1687/25, fig. 4) shows a c. 28 μm thick layer of lead white, very fine yellow ocher, and very little finely ground ultramarine. The yellow paint is sitting on a c. 5 μm underpaint of charcoal black with a little



5. Paint cross section of sample 1687/26, background to the left of the forehead. (1) ground; (2) c. 12 μm bone black; (3) c. 28 μm translucent green layer, containing weld (luteolin, HPLC), chalk, a little red ocher, indigo. Magnification 305x

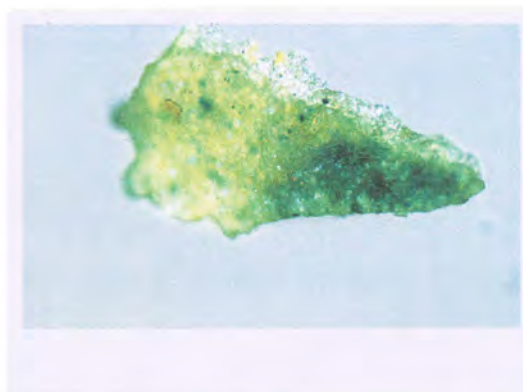


6. Paint cross section of sample 1687/26. Fluorescence. Magnification 305x

yellow-brown ocher, a little lead white, and chalk in the same brown medium. In both samples the light-colored ground can be seen underneath the dark underpaint.

Paint samples from the drapery in the *Girl with a Pearl Earring* show that greenish, bluish, and reddish shadows were made by adjusting the hue of the main pigment by color mixing. In some of the samples there is an indication that organic red in the mixture with ultramarine has faded. The shadow of the jacket may have had a more reddish tone. There was not sufficient sample material to identify the organic red in the *Girl with a Pearl Earring*. In Vermeer's *The Love Letter* (Rijksmuseum, Amsterdam), an organic red was identified as cochineal, a dye made from the insect *Coccus cacti*.

It became clear from the paint cross sections that Vermeer applied a rather translucent final paint layer, especially in the shadows. These samples derive from areas where the shadow meets the background and where the picture is "difficult to read." The edge of the figure seems blurred; it is not altogether clear where the figure stops and the background starts. This soft outline is achieved by a gradual change in composition of the top paint layer. Toward the transition between the clothing and the background, other pigments were used and the final paint was applied more and more in a glazing way. There is one layer of a translucent glaze, with little coloring matter and rich in medium. Samples from the back of the girl's neck (1687/24) and along the back below the headdress (1687/23) show only a few particles of ultramarine, bone black, and lead white in a medium-rich, yellowish-brown paint layer. SEM-EDS and Fourier Transform



7. Fragment of sample 1687/26 in incident and transmitted light. Magnification 124x

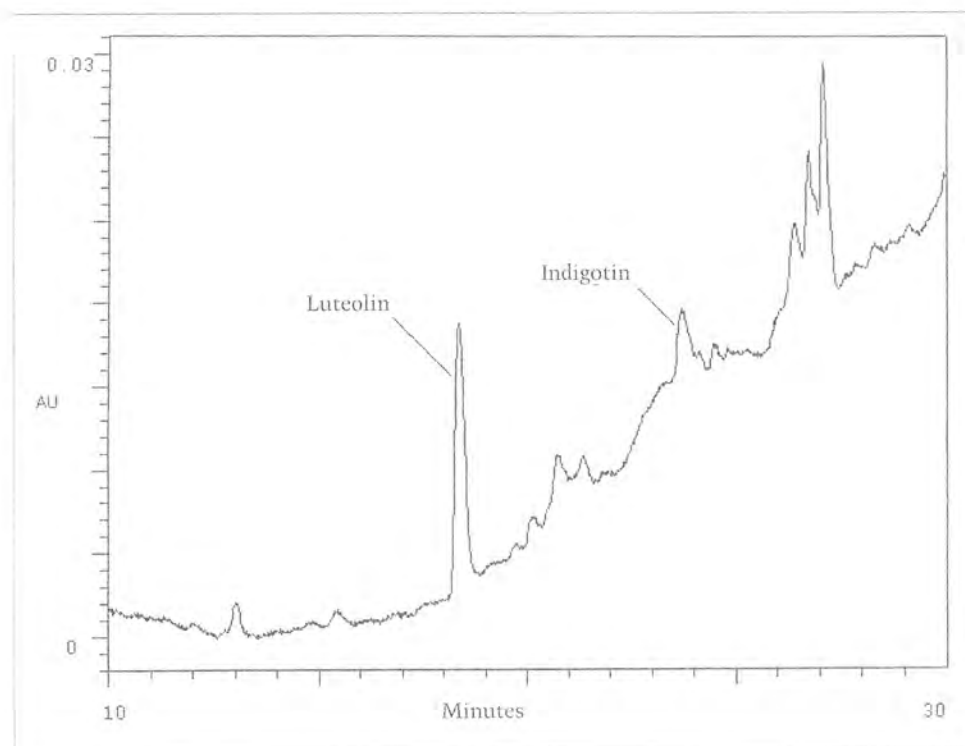
Infrared Spectroscopy (FT-IR) analyses proved the glaze to have a high content of alumina and chalk, indicating the former presence of now discolored organic pigments. Reasons for adding chalk to organic pigments were its use as a cheap bulking agent or as an absorbent (see below, "Paint Layer of the Background").

Paint Layer of the Background

At present, after the 1994–1995 restoration, the background still appears uneven. Various degrees of gloss are apparent, especially on the left-hand side of the picture; a dull, milky-grayish green is variegated by seemingly saturated darker spots. Examination with the stereomicroscope shows that the paint looks saturated in the original dark patches that appeared during removal of the old retouchings. This is in contrast to the rest of the background, where the paint looks washed-out, matte, and milky. The old retouchings have obviously shielded these parts from moisture and light.

The top paint layer in the background

8. HPLC-chromatogram of sample 1687/19 from the background on the right-hand side of the picture. The retention time, read from the horizontal axis, is for luteolin 18.370 and for indigotin 23.720 minutes. The three components with retention time around 27 minutes could not be identified. Additional UV-vis-spectra showed that, in contrast to luteolin and indigotin, the unknown components are colorless. As the sample comprised pigment, binding medium, and possibly some varnish, the peaks are probably due to organic material other than pigment.

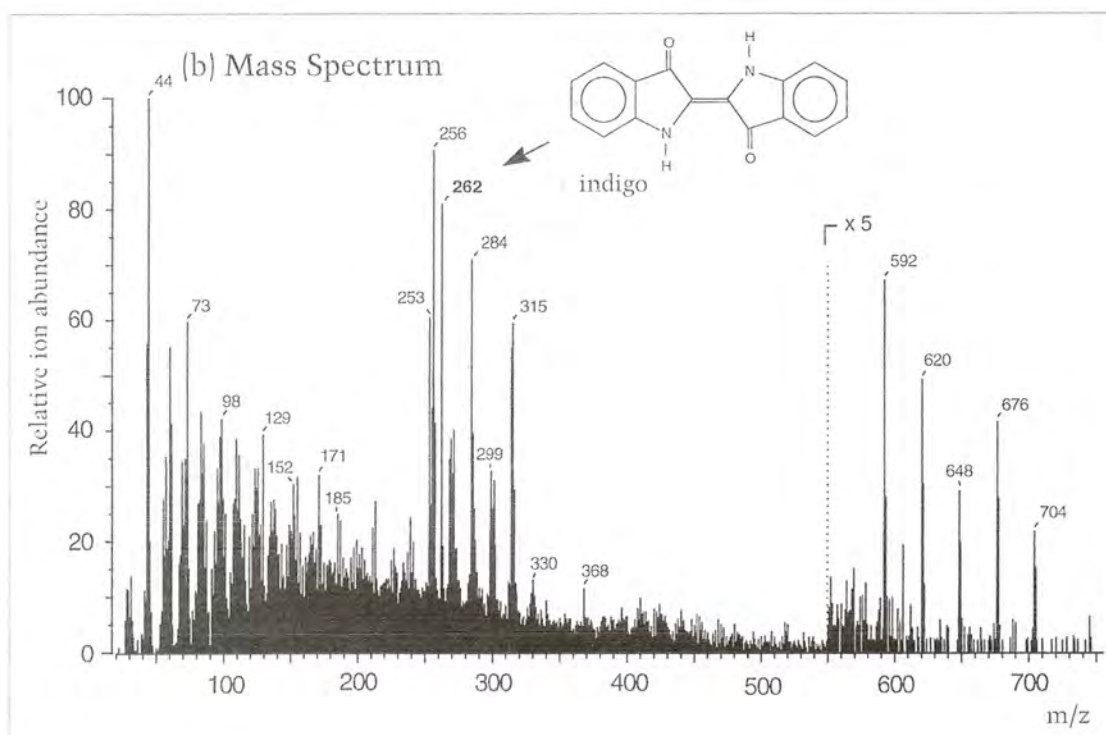
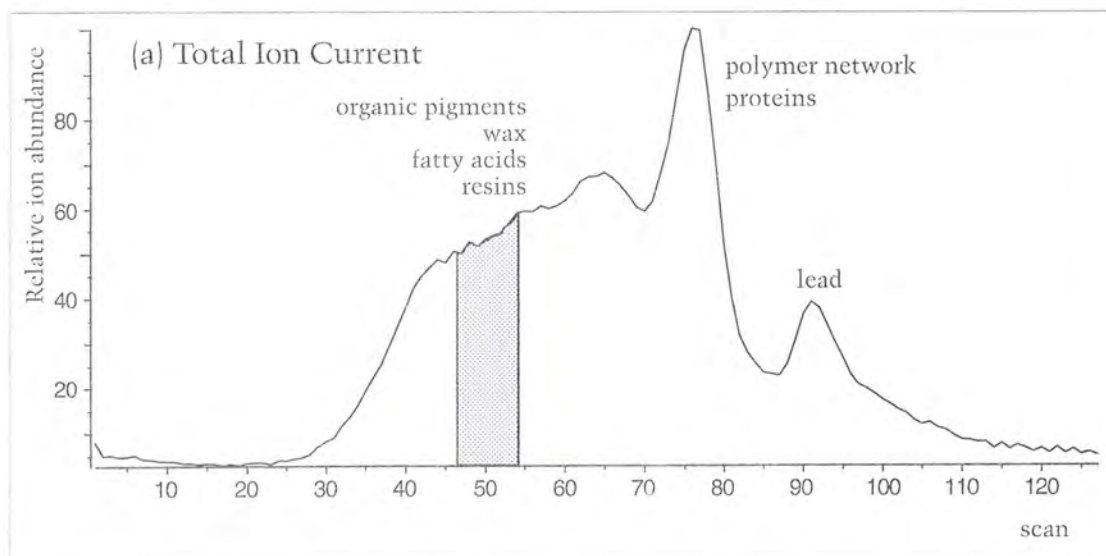


is remarkably transparent. Under the microscope, the translucent layer appears greenish in a sample from the left-hand side of the picture (1687/26) and slightly yellowish-brown-green in a sample from the right (1687/19 and 21). From microscopic observation of the cross sections it was not immediately obvious what pigments constitute the translucent, murky green paint. In transmitted light a bright yellow and in ultraviolet light a fine blue were observed (1687/26, figs. 5–7). Wet-chemical analysis indicates the presence of indigo and a yellow dye. This was confirmed by using high performance liquid chromatography (HPLC), which positively identified the presence of both indigo (1687/19) and luteolin (1687/19 and 26) (fig. 8). Luteolin, a tetra-hydroxy-flavone, is the coloring matter of weld. The presence of indigo was confirmed by Direct Temperature-Resolved Mass Spectrometry (DTMS) (1687/31 and 34; fig. 9). Both organic pigments are present in the left-hand and right-hand sides of the background of the picture. In addition, linseed oil was deter-

mined as the binding medium (p/s ratio = 1.7) with py-TMAH-GCMS.

A mixture of indigo and weld, both being organic colors, results in a rather translucent green paint layer. Weld, in Dutch *wouw* or *woude*, is a natural yellow dyestuff, obtained from the cultivated herbaceous plant Dyer's Rocket, *Reseda luteola* L. It is the oldest European dyestuff and the oldest yellow dye plant in the world.¹³ Weld was used for dyeing silk and woolen materials as well as for making paints. In the seventeenth century in Holland the expression "wel geblaut, wel gewaut" was used, meaning well-dyed with blue (indigo) and well-dyed with yellow weld.

For use in a painting, the dye must be insoluble. Unlike indigo, weld is soluble in oil and therefore must be precipitated onto a substrate. Microscopic analysis, FT-IR, and SEM-EDS showed that the glaze of the background also contains a high proportion of chalk, alum, a little lead white, a little red ocher, and some proteinaceous material (1687/26).¹⁴ The finding of these organic pig-



9. DTMS-spectrum of sample 1687/31 found on top of the paint layer in the background, top right. Ground + dark paint + some varnish. (a) The TIC (Total Ion Current) spectrum can be regarded as a summation of mass spectra from components that have evaporated from the filament at different temperatures. This TIC comprises three main temperature regions: the volatile organic substances (organic pigments, waxes, fatty acids, and resins), the polymer network, and inorganic substances (lead white). (b) In the spectrum from the low temperature region (scan 46–54, the region indicated in the TIC), several peaks can be observed, indicating the presence of indigo (m/z [mass to charge] 262), palmitic acid (m/z 256), stearic acid (m/z 284), dicarboxylic acids such as azeleic acid (dic9) (m/z 98, 152), beeswax (m/z 368, 592, 620, 648, 676, 704), and highly oxidized abietic acids (m/z 253, 299, 315, 330). In higher temperature regions (not shown here), proteins and lead are identified.

ments together with chalk and alum agrees rather well with written sources, for example, the *Secret-Boeck* of 1609: "Take weld, which in Latin is called Flortinctorius; they are the yellowish flowers used by the cloth dyers. Take the stems and the flowers together, as many as you want. Make chalk-water (lime) and pour it over the flowers in a large kettle.

Leave it to boil for such a long time that the yellowness of the flowers may be extracted."¹⁵ The court physician Théodore de Mayerne remarked in 1620 that weld gets its body from chalk and its color from a plant. For manufacturing the pigment, he says that the dye has to be precipitated first onto alum and then kneaded with chalk.¹⁶

The paint layer in the background of the *Girl with a Pearl Earring* gets its "body" from chalk. To produce an insoluble pigment from weld, a metal salt is needed to form a metal-flavone complex that is insoluble and colored. The pigment is the yellow precipitate formed when alum is added to the weld extract.¹⁷ Besides its presence as a mordant for weld, alum could be present as a substance to make the paint glossy. Indeed, De Mayerne advises mixing indigo and other organic pigments with powdered alumstone and nut oil, because the colors will be much more "oriental," which Johannes van de Graaf translated as "glossy." According to De Mayerne, the color will also be more durable.¹⁸

Weld extract yields the purest and fastest yellow shade of all natural yellow dyes. The bright yellow was still visible, seemingly unchanged inside the paint sample.¹⁹ The yellowish-brown-green color on the right-hand side of the painting (1687/19 and 21) may be explained by partial discoloration of indigo. Some typical oxidation products of indigo, such as isatine, could not be detected, however. The other ingredients—chalk, alum, ocher, and bone black—are all stable materials.

Originally the background must have been made with a smooth, glossy, hard, translucent green paint, which was made to look darker and given depth by a dark underpaint. In addition to the factors mentioned at the beginning of this section, partial discoloration of the indigo may have added to the unevenness of the background.

Traces of Former Restoration Procedures

The painting has undergone at least five different types of restorations, some of which have been documented:²⁰ (1) starch lining (Van der Haeghen, 1881) and probably consolidation procedures at the front with glue; (2) wax-resin lining (Traas, 1960); (3) "regeneration" with alcohol vapors and probably copaiba balsam (De Wild, 1915, 1922); (4) retouching of the paint (Traas, 1960; Jørgen Wadum, 1994); (5) cleaning and varnish removal (De Wild, 1915; Traas, 1960; Wadum, 1994). The possible effects of some of these restorations on paintings are discussed in this section. In addition, results of chemical analysis are presented to illustrate that these procedures

may change the chemical composition of a painting.

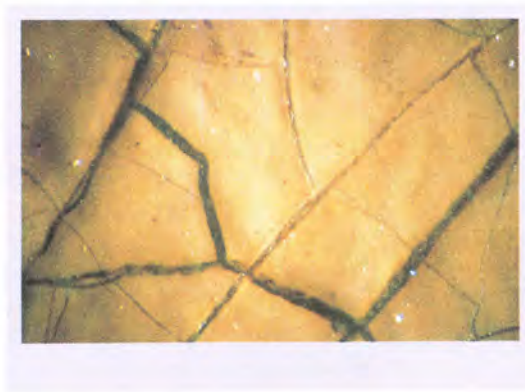
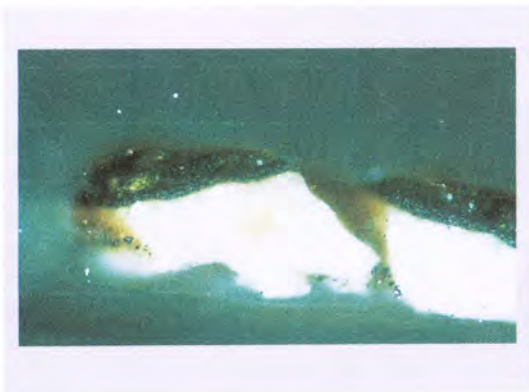
Lining

Linings with starch adhesives or animal glue make paintings vulnerable to both "regeneration" methods and aqueous treatments, since alcohol and water cause swelling of the glue. Swelling and successive contraction of the glue may cause flaking of paint layers.²¹ Aqueous lining methods have not been used in the Netherlands very frequently. Consolidation of flaking paint with animal glue may also be done separately.

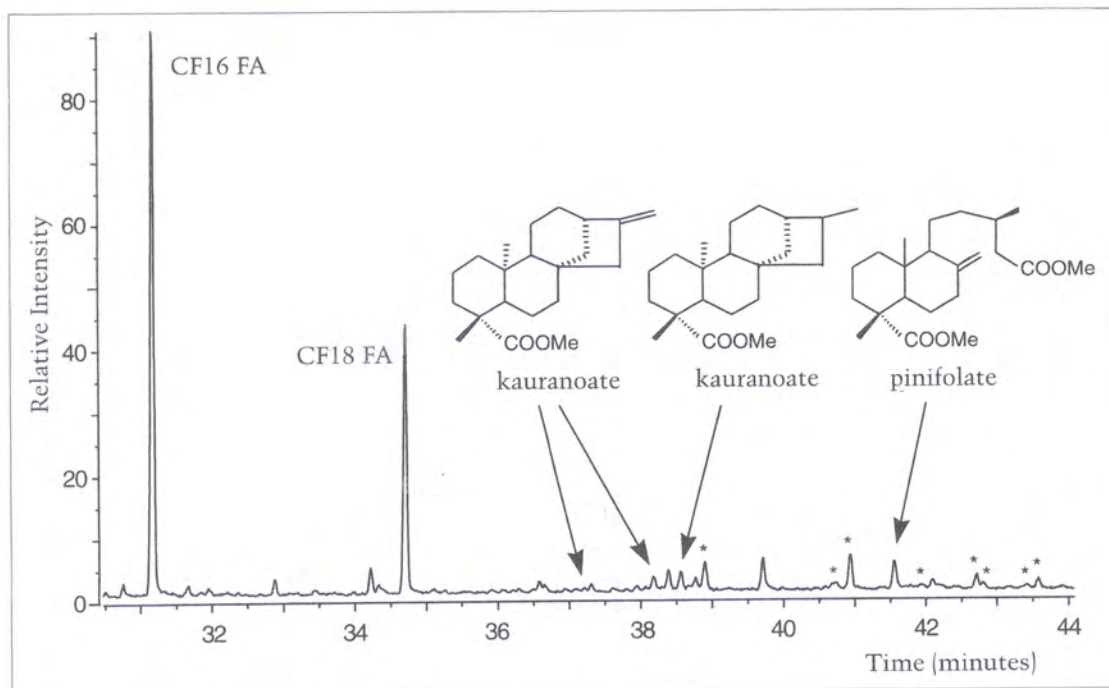
HPLC analysis of the black substance in the cracks in the forehead and cheek of the girl (1687/18) and black material from the edge of cupped paint in her chin (1687/38) revealed the presence of hydroxyproline, indicating an animal glue. The ratio alanine/proline > 1 may indicate a fish glue.²² This seems to be confirmed by staining techniques (amido black, acid fuchsine). Paint layers and ground have been stained only slightly positive. From the cross section it can be observed that the glue has pushed black particles from the black underlayer down into the cracks (fig. 10). The dark underlayer does not seem to be softened by this action. Clearly the animal glue was used for consolidation of flaking paint.

Wax-resin lining was common practice in the Netherlands since the last century. The lining material was often made by melting beeswax with colophony, and usually Venice turpentine was added to improve the flexibility of the lined painting.²³ The application of the wax-resin mixture to the reverse of the painting took place with physical pressure, using hot irons. The molten substance was partly forced through the cracks to the front of the painting. Evidence that wax can also migrate *into* the paint itself has been obtained very recently by Jaap Boon and others.²⁴ Because of the reputedly bad effect of this method on paintings and because of the development of less invasive modern lining techniques, it is rarely applied now.²⁵

The wax-resin mixture applied by Traas in 1960 (1687/2) was analyzed with DTMS and PY-TMAH-GCMS. It was found to consist of beeswax and a pine resin (colophony) in relative amounts of roughly 2:1. No evidence for the use of Venice turpentine was found. The relative amounts of abietic acid (AA),



10. Paint cross section of sample 1687/34, found on top of the paint layer top left, above the signature. Overexposed in order to show the dark paint layers. From bottom to top, one can see the light-colored ground, the dark underlayer, and the varnish and glue. The glue has pushed down the black particles into the paint cracks on the left and in the middle of the sample. Magnification 124x



11. Detail of *Girl with a Pearl Earring* showing the cracks containing the black material in the girl's face. Microphotograph made with an operation microscope. Magnification 8.9x

12. PY-TMAH-GCMS partial chromatogram of the ground layer of sample 1687/33. The various peaks represent the methyl esters of palmitic acid (C16) and stearic acid (C18), due to linseed oil, and of pinifolic acid, kauranoic acid, and two isomers of kaurenoic acid, demonstrating the presence of copaiba balsam. In addition, some highly oxidized abietic acids (marked *) have been identified.

dehydroabietic acid (DHA), 7-oxo-DHA, and 15-hydroxy-7-oxo-DHA are about 2:60:27:11.²⁶ The degree of oxidation of the resinous fraction is relatively low and reflects the relatively young age and the absence of light and oxidizing (metal-containing) catalysts.

No indication for beeswax was found from chemical analysis of dislodged samples (1687/33, 34), material from cracks (1687/18), and old varnish (1687/32), indicating that the influence of the wax-resin lining on the painting may have been limited. The only exception is the ground layer from sample 1687/31, also a dislodged paint sample, which was found to contain some beeswax (fig. 9).

Regeneration

The regeneration of blanched varnishes was generally achieved by exposing the surface of the painting to alcohol vapors, but occasionally, especially when oil varnishes were involved, a combination of alcohol vapors and copaiba balsam was used. An extensive study of this method, commonly referred to as the Pettenkofer method—its use, history, and effects on paintings—was carried out by Sibylle Schmitt.²⁷ In the Netherlands, the use of copaiba balsam for restoration purposes is documented, for example, in the archives of the Mauritshuis and the Frans Hals Museum and in a treatise on drying oils by the chemist G. J. Mulder.²⁸



13. *Girl with a Pearl Earring*, schematic photograph indicating the provenance of the samples
 Photograph by Jørgen Wadum, Royal Cabinet of Paintings Mauritshuis, The Hague

The negative effects of copaiba balsam on paintings were already noticeable when the balsam came into extensive use at the end of the nineteenth and the beginning of this century. Chemical investigations were later done,²⁹ and warnings against the use of copaiba balsam are frequently found.³⁰ Copaiba balsam causes softening, darkening, and swelling of the paint and migration of components, as has been described by Hans Brammer³¹ and Schmitt.³² Copaiba balsam, an oleoresin obtained from *Leguminosae* trees of the genus *Copaifera* in South America, was identified in the brownish-black material that extruded from the cracks (1687/18) in the forehead and cheek of the girl (fig. 11).³³ It was also found in the ground layer of a dislodged fragment in the background around the signature (1687/33), but not in the paint layer of the glaze (1687/34). Small amounts of balsam, in addi-

tion to linseed oil and highly oxidized abietanes,³⁴ have been detected in an old varnish underlying some retouchings (1687/32). No copaiba balsam was found in the wax-resin relining material (1687/2). This means that the balsam was probably introduced by some surface treatment before the restoration by Traas in 1960. We assume that the copaiba balsam was used in one of the "regeneration" treatments by Derix de Wild in 1915 or 1922.³⁵

The methyl esters of pinifolic acid, kauranoic acid, and two isomers of kaurenoic acid were identified by PY-TMAH-GCMS (fig. 12). The combination of these diterpenoid acids is characteristic for copaiba balsam obtained from *Copaifera langsdorfii* L.³⁶ This type of copaiba balsam has also been found in other paintings, where it has been used for regeneration or as an addition to the paint medium.³⁷ No softening of paint layers, nor any other visible effect known to be induced by copaiba balsam, was observed.

Conclusions

Microscopic examination of paint cross sections in combination with SEM-EDS, FT-IR, HPLC, DTMS, and PY-TMAH-GCMS has shed new light on the painting techniques used by Vermeer in the *Girl with a Pearl Earring* and on the effects of former restoration techniques. On a thick, light-colored ground, Vermeer laid down the composition of the picture in dark paint of brown and black tones, possibly after sketching the figure in charcoal black. The monochrome bone black-containing underpaint was applied in a thin layer in areas that Vermeer intended to be dark in the final painting. In the lighter parts, he thinly brushed a lighter paint mixture of charcoal mixed with yellow and brown ocher. For the final execution, he applied a single layer of paint for the different colored areas in both the figure and the background. In creating the image, he gradually changed the pigment mixture while moving from the figure to the background (or vice versa). While changing the pigment mixture, Vermeer chose organic pigments that could be used in a glazing way, that is, in a medium-rich paint.

In the girl's blue drapery, ultramarine was the main constituent, mixed with a yellow ocher, an organic red, and some lead white. To obtain different tones in the yellow jacket,

very finely ground yellow ochre was mixed with some lead white and ultramarine. The pigments responsible for the greenish hue of the background are indigo and weld, a dye frequently used in the Netherlands.

It is not possible to cite a particular treatment as the reason for the present appearance of the background. Restorations, partial coverage of the paint by retouchings, darkening of the linseed oil-rich medium, and partial discoloration of the indigo may have contributed. In the past, the picture has undergone several treatments with water and glue, alcohol, and copaiba balsam. Fish glue has been observed and is probably a remainder of treatments to consolidate the paint from the front. In addition, copaiba balsam from the South American tree *Copaifera langsdorfii* L. was found in various parts. From our study we conclude that the effects of copaiba balsam on the physical properties of the paint layers are probably limited. The same can be said of the wax-resin lining applied in 1960, from which only traces of beeswax have been found.

The complicated restoration history and the fact that we are dealing with a delicate and precious painting make it very difficult to

point to one particular treatment as the reason for the appearance of the background. Results from various tests, however, point to the treatments that involved water, more specifically to the water-based lining from 1881 and the consolidation of cupping paint with fish glue. Swelling and later contraction have broken up the paint layer so that it no longer works as a glaze.

The main purpose of this detailed study of the background of the *Girl with a Pearl Earring* was to determine its original appearance. As a side effect we found materials that shed light on Vermeer's technique. The background of the painting was originally of an even, smooth, glossy, translucent, hard green paint, made to look darker and given depth by a dark underpaint. The surface of the paint has since been altered by the effects of light and moisture. Vermeer obviously wanted to place the girl against a background different from those of *The Milkmaid*, for instance, and *The Girl with the Red Hat*. He wanted to convey a perfect illusion of a precious object made of enamel. This scientific examination has shown that even the painting technique of the background was adapted for this purpose.

APPENDIX 1

List of Samples Discussed in the Text (fig. 13)

Analyses other than microscopic observations are indicated. The samples were taken by Karin Groen (KG) and Jorgen Wadum (JW). Symbols used are as follows: Δ = dislodged fragment found on top of the surface; $^{\circ}$ = sample removed from the paint layer; * = restoration materials.

*1687/2 (KG) Wax-resin lining mixture, right-hand edge, 9 cm from below. PY-TMAH-GCMS: beeswax, oxidized pine resin.

Δ 1687/4 (JW) Original pink paint, dislodged, on top of the paint at the right-hand side in the background. Incomplete sample; one layer, c. 50 μm thick, lead white and possibly vermilion.

* $^{\circ}$ 1687/18 (JW) Black material from the broad cracks in forehead and cheek, possibly some varnish present in the sample as well. PY-TMAH-GCMS: linseed oil ($v/s = 1.8$), oxidized abietanes, and copaiba balsam.

$^{\circ}$ 1687/19 (KG) Along the right-hand edge 4.1 cm from below. (1) >70 μm ground; (2) c. 10–24 μm bone black in brownish-black layer; (3) c. 24 μm translucent yellowish-brown layer, contains chalk, a little lead white, indigo (HPLC), luteolin (HPLC).

$^{\circ}$ 1687/21 (KG) Background, bottom right, 1.3 cm from below, 1.2 cm from the right-hand side. (1) glue; (2) c. 100–200 μm ground layer, containing lead white, chalk, a little brown and red ocher, very little fine black; (3) c. 10 μm bone black in brown medium; (4) c. 20 μm translucent brown layer containing chalk, a little lead white, indigo (wet-chemical test), a little red and yellow ocher, a little black, possibly organic yellow.

$^{\circ}$ 1687/22 (KG) Shadow in blue drapery, right-hand side, 6.0 cm from the bottom edge of the picture, 4.1 cm from the right-hand side. (1) >22 μm ground; (2) c. 7 μm bone black in grayish-brown medium; (3) 0–8 μm bone black, very little brown ocher in brown medium; (4) c. 40 μm natural ultramarine, carbon (bone?) black, very little of an organic red pigment, a little yellow and brown ocher.

$^{\circ}$ 1687/23 (KG) Edge of girl's blue turban, 25.5 cm from below, 11.5 cm from the right-hand side. (1) ground layer missing in sample; (2) bone black in brown medium; (3) c. 27 μm grayish translucent layer, contains chalk, very little ultramarine, very little organic red pigment.

$^{\circ}$ 1687/24 (KG) Sample from the neck of the girl, 22.0 cm from below, 12.8 cm from the right-hand side. (1) ground; (2) c. 8 μm a little bone black in brown medium; (3) c. 4 μm bone black, brown medium; (4) chalk, a little ultramarine, very little fine red and yellow iron oxide, and bone black in medium-rich, light yellowish-brown medium.

$^{\circ}$ 1687/25 (KG) Yellow jacket, bottom edge, 14.9 cm

from the left. (1) ground, contains lead white, chalk, very little brown and red ocher, very little very fine black; (2) c. 5 μm a dark layer of yellow, brown, and very little red ocher, a little finely ground charcoal black in brown medium; (3) c. 28 μm lead white, finely ground yellow ocher, very little brown ocher, and finely ground ultramarine.

$^{\circ}$ 1687/26 (KG) Background to the left of the forehead. (1) ground; (2) c. 12 μm bone black; (3) c. 28 μm translucent green layer, containing weld (luteolin, HPLC), chalk, a little red ocher, indigo.

$^{\circ}$ 1687/28 (KG) Highlight in the yellow cloth, cascading from the turban, 34.4 cm from the bottom edge, 10.4 cm from the right. (1) ground; lead white, chalk, a little yellow ocher, and black; (2) c. 2 μm black pigment, possibly finely ground charcoal, in brown medium; (3) c. 24 μm lead white, finely ground yellow iron oxide.

Δ 1687/31 (JW) Paint found on top of the paint layer in the background, top right. Ground + dark paint + varnish. (DTMS:) indigo, linseed oil ($v/s = 1.3$), some beeswax, highly oxidized abietanes, proteins, lead.

*1687/32 (JW) Scraping from the very brown varnish near the top edge of the painting, since 1960, perhaps longer, covered by extensive overpaint. Linseed oil ($v/s = 1.6$) and highly oxidized abietanes (DTMS and PY-TMAH-GCMS), copaiba balsam (PY-TMAH-GCMS), lead (DTMS).

Δ 1687/33 (JW) Ground + paint found on top of the paint layers, top left, below the signature. Ground: linseed oil ($v/s = 2.1$), copaiba balsam, highly oxidized abietanes (PY-TMAH-GCMS).

Δ 1687/34 (JW) Sample (ground + paint + varnish) found on top of the paint layer top left, above the signature. Paint: linseed oil ($v/s = 1.7$), relatively high C8/C9 diacid concentration (PY-TMAH-GCMS). Whole sample, DTMS: indigo, linseed oil, lead.

* $^{\circ}$ 1687/38 (JW) Black material from the edges of cupping paint on the chin of the girl. Fish glue (HPLC); carbon (bone?) black.

APPENDIX 2

Experimental Section

The analyses were performed at the Netherlands Institute for Cultural Heritage (ICN) and the FOM Institute for Atomic and Molecular Physics (AMOLF) in Amsterdam, and DSM-Research in Geleen.

Microscopy

Samples were embedded in polyester resin, and after grinding and polishing were examined under the MOLART Leica Research microscope DMRX at the ICN. Magnification up to 1,000x. Incident UV-light from a high-pressure mercury vapor lamp. Filterblock "violet" BP 355–425, RKP 455, LP 460. Thin microscope slides were examined in polarized transmitted

light. For interpretation of the results obtained with SEM-EDS (see below), additional wet-chemical analyses were performed on samples 1687/18, 19, 21, 22, and 26.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)
SEM-EDS was performed with Philips SEM 515 and EDAX PV 9800 at DSM-Research. Electron beam 20 kV. Samples were coated with carbon to give the back-scattered image and for identification of the elements.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was performed at DSM-Research with a Bruker IFS85 with an IR-microscope attached.

High-Performance Liquid Chromatography (HPLC)

The analyses of the organic dyes and the proteins were carried out with HPLC at the ICN. Experimental setup: Waters 616 HPLC-pump; Waters PDA 996 detector (detection wavelength 254 nm); Waters 717 Auto Sampler. Columns: (organic dyes) Spherisorb ODS-2 3 mm, 100 mm x 4.6 mm; (proteins) Supelcosil LC 18DB.

HPLC of the organic dyes was performed employing a procedure according to Jan Wouters and Noemi Rosario-Chirinos.³⁸ Sample preparation involved hydrolysis of the sample with a water/methanol/36% HCl reagent. Separation was achieved using the following elution program. 66A/24B/10C: 2 minutes, linear gradient to 0A/90B/10C: 3 minutes. The eluent consisted of (A) water, (B) methanol, (C) H_3PO_4 5% w/v in water. The flow was 1.2 ml/min.

HPLC of the proteins was performed with the procedure described by Peter Janssen and others³⁹ and involved hydrolysis of the sample with 6N HCl to the free amino acids and derivatization with phenylisothiocyanate (PITC). The elution program started with 20A/76B/4C in 25 minutes to 20A/40B/40C and then in 1 minute to 10A/10B/80C for another 4 minutes. The eluent consisted of (A) 0.7 M NaOAc + 2.5 ml TEA with HAc (pH 6.4), (B) water, (C) acetonitrile.

Pyrolysis-TMAH-Gas Chromatography Mass Spectrometry (Py-TMAH-GCMS)⁴⁰

Py-TMAH-GCMS was performed at AMOLF. Samples of typically 5–10 μ g were homogenized in a mini glass mortar and made into a suspension with a few μ l of a 2.5% solution of tetramethylammonium hydroxide (TMAH) in water. Aliquots of this suspension were applied to the analytical filament (Curie point 610°C) and dried *in vacuo*. Subsequently, the sample wire was inserted into a glass liner, flushed with argon, and placed in the pyrolysis chamber (190°C).⁴¹ The more volatile (methylated) components evaporate under these conditions and are cold-trapped in the first part of the column. Inductive heating (610°C)

with an RF field is used to pyrolyze the remaining material.

GCMS data were obtained using a fused silica SGE BPX5 column (25 m, 0.32 mm i.d., 0.25 mm film thickness) in a Fisons gas chromatograph (series 8565 HRGC MEGA 2) coupled directly to the ion source of a JEOL DX-303 double-focusing (E/B) mass spectrometer. Helium was used as the carrier gas at a flow rate of approximately 2 ml/min. The initial temperature of the gas chromatograph was 40°C. The oven temperature was programmed with a ramp of 6°C/min. Ions were generated by electron ionization (70 eV) in an ionization chamber, accelerated to 3 keV, mass separated and postaccelerated to 10 keV before detection. The mass spectrometer was scanned from m/z 40–700, with a cycle time of 1 s. A JEOL MP-7000 data system was used for data acquisition and processing.

Direct Temperature-Resolved Mass Spectrometry (DTMS)⁴²

DTMS experiments were performed at AMOLF. Samples of typically 10 μ g were homogenized in a mini glass mortar and made into a suspension with a few μ l of water or ethanol. Aliquots of the suspension were applied to a Pt/Rh (9/1) filament (100 μ m diameter) of a direct insertion probe and dried *in vacuo*. Subsequently, the probe was inserted into the ion source (200°C) of a JEOL SX-102 double-focusing mass spectrometer (B/E). The filament was temperature programmed at a rate of 0.5 A/min, corresponding to about 6°C/s, to an end temperature of about 800°C. Molecules evaporated from the filament were ionized (16 eV) and accelerated to 8 keV. The mass spectrometer was scanned from m/z 20–1,000, with a cycle time of 1 s. A JEOL MP-7000 data system was used for data acquisition and processing.

NOTES

The authors of this study are involved in Molecular Aspects of Aging in Art (MOLART), a five-year joint project of Dutch art historians, conservators, chemists, and physicists. The project focuses on determining the present condition of works of painted art produced from the fifteenth to the twentieth century. MOLART comprises studies, for example, on the history of Dutch painting restoration. Emphasis is put on molecular-level studies using (spatially resolved) mass spectrometry, 2D-microscopy, and infrared and Raman spectroscopy. Special attention is paid to indicators of aging processes such as the degree of oxidation of terpenoids in resins, lipids, and proteins.

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2. Hermann Kühn, "A Study of the Pigments and the Grounds Used by Jan Vermeer," in *Reports and Studies in the History of Art*, National Gallery of Art (Washington, 1968), 154–202.
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5. *Nieuwe Courant*, 2 March 1903: "in een allertreurigsten staat van verwaarlozing."
6. Archive Mauritshuis (1903), corr. no. 62, signed "A. Bredius."
7. Archive Mauritshuis (1915), corr. nos. 218, 225 and (1916) no. 83.
8. Wadum et al. 1995, 24–25.

9. Wadum et al. 1995, 18 and nn.20, 21.
10. Rutherford J. Gettens, Hermann Kühn, and W. T. Chase, "Lead White" in *Artists' Pigments*, ed. Ashok Roy [National Gallery of Art] (Washington, 1993), 68.
11. The p/s (palmitic/stearic) ratio may give information on the type of medium that has been used. A p/s ratio of 1–2 is typical for linseed oil (John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, 2d ed. (London, 1994), 33. The ratio is relatively high in the sample (1687/33) of the ground layer, possibly owing to the presence of traces of additives. Beeswax is mainly composed of esters of palmitic acid (p) and long chain alcohols and as such is a good candidate for raising the p/s ratio. However, in this particular sample it has not been identified. See "Traces of Former Restoration Procedures."
12. Ralph Mayer, *The Artist's Handbook of Materials and Techniques* (London, 1972), 43. For examples see, for instance, the essay of Karin Groen and Ella Hendriks, "Frans Hals: A Technical Examination," in Seymour Slive, ed., *Frans Hals* [exh. cat., Royal Academy of Art, National Gallery of Art, and the Frans Hals Museum] (London, Washington, and Haarlem, 1989), 108–127.
13. Judith H. Hofenk-de Graaf, *Natural Dyestuffs. Origin, Chemical Constitution, Identification*, ICOM Triennial Meeting (Amsterdam, 1969), 1.
14. In the sample from the bottom right-hand corner a trace of copper was found as well, although no copper pigment could be seen. Kühn, in his 1966 examination, using x-ray diffraction, identified copper-acetate in the transparent layer. Perhaps a copper compound was used as a dryer.
15. Carel Batin, *Secreet-Boeck, waerin vele diversche secrete ende heerlicke consten, in veelderleye materien . . .* (Dordrecht, 1609). See also Agenitus Martin de Wild, *The Scientific Examination of Pictures* (London, 1929), 85 n.1.
16. The De Mayerne manuscript is in the British Museum, London. See Johannes Alexander van de Graaf, "Het De Mayerne manuscript als bron voor de schildertechniek van de Barok" (Ph.D. diss., Rijksuniversiteit Utrecht, Mijdrecht, 1958), 151, no. 32.
17. It is possible that the pigment was made from woolen textiles dyed with weld, as was common practice in the seventeenth century in Holland. The presence of proteins in the paint layer could therefore also be explained as being from tiny wool fibers. Judith Hofenk-de Graaf, verbal communication.
18. Van de Graaf 1958, 173, no. 65.
19. De Wild (1929) suggests that in the *View of Delft* and *The Little Street* a yellow glaze has disappeared from the leaves. This is probably another yellow pigment. Tests carried out by Jo Kirby and David Saunders indicate that lakes prepared directly from the raw material are more lightfast than those prepared indirectly from cloth shearings; David Saunders and Jo Kirby, "Light-Induced Colour Changes in Red and Yellow Lake Pigments," *National Gallery Technical Bulletin* 15 (1994), 79–97.
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21. Adam Karpowicz, "In-plane Deformations of Films of Size on Paintings in the Glass Transition Region," *Studies in Conservation* 34 (1989), 67–74.
22. Raymond Heesters, Judith Hofenk-de Graaf, and Wilma Roelofs, *Onderzoek naar de identificatie van proteïne bindmiddelen met HPLC van PTC-aminozuurderivaten*, internal publication of the Netherlands Institute for Cultural Heritage (Amsterdam, 7 January 1996), 6.
23. In many other wax-resin samples from Dutch paintings, for example, from *View of Delft* which was lined by Willem Antonij Hopman in the Mauritshuis in 1870, we determined Venice turpentine as an oleoresin (Klaas Jan van den Berg, unpublished results).
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28. G. J. Mulder, "De scheikunde der droogende olicen en hare toepassing," in *Scheikundige verhandelingen en onderzoekingen* (Rotterdam, 1865).
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30. C. Jantsch, "Rückblicke und Ausblicke zur Entwicklung der heutigen Restaurierungstechnik," *Technische Mitteilungen für Malerei* 21 (1939), 164.
31. Hans Brammer, "Durch Restaurierungsmaßnahmen beschädigte Gemäldeoberflächen: 2 Beispiele aus der Kassler Gemäldegalerie," *Zeitschrift für Kunsttechnologie und Konservierung* (1987), 1:95–104.
32. Schmitt 1990.

33. Wadum et al. 1995, 21.
34. The oxidation state of the diterpenoid abietane acids was extremely high and determined to be 0:5:26:69, according to Van den Berg et al. 1996.
35. Derix de Wild had regenerated varnishes (Mauritshuis archives: 1915 "Schoongemaakt, geregeerd en governist door Derix de Wild"). He must have been familiar with the use of copaiba balsam for these purposes. His son, the scientist Agenitus Martin de Wild, devoted a large part of the chapter called "The Restoration and Conservation of Paintings" in his book (1929, 83–88) to the treatment of blanched varnish layers. The purpose of this exercise was to make the image clearly visible again without having to remove the varnish layer. He is skeptical about the use of copaiba balsam in this treatment because of its temporary effect. In addition, the varnish darkens very quickly, changing the color balance of the underlying picture.
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